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16. ABSTRACT The report gives results of a 3-year program to assess the environmental impact of petroleum refining atmospheric emissions. Fugitive and process emissions were extensively sampled at 13 refineries in the U.S. Nonmethane hydrocarbon emission rates were measured from valves, flanges, pump and compressor seals, process drains, relief valves, cooling towers, and wastewater treating units. Flue gases were sampled from fluid catalytic cracking units, sulfur recovery processes, process heaters, and other process units. Their compositions were determined. Organic species in liquid streams and emitted vapor were identified and quantified. Sampling and analytical methods are described. Emission factors for major fugitive emission sources were calculated. Nomographs were developed showing the relationship of hydrocarbon concentrations at leaking sources (screening values) with the leak rates from the sources. Existing and available emission control technologies for refinery emissions sources are evaluated. Control methodologies are recommended for individual emission sources. The impact of refineries on the surrounding atmosphere and population is estimated.

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by

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1.0 INTRODUCTION

This three year refinery assessment program was conducted by Radian Corporation under EPA Contract Nos. 68-02-2665 and 68-02-2147, Exhibit B. The assessment report is being issued in five volumes. Volume 1 contains the main body of the report. Volumes 2 - 5 contain six appendices to the report.

This volume, Volume 1, contains eight major sections plus the reference section and conversion table (English units to metric units). Section 1, Introduction, contains a listing of the program objectives and a description of earlier studies of environmental impacts of petroleum refineries. The major conclusions of the current program and the significant results which support the conclusions are presented in Section 2. Emission control options recommended for refinery emission sources are listed in Section 3 of this report.

The major segments of the refinery assessment report can be logically separated into two major parts, Part A and Part B. Part A contains the description and results of the field measurement activities. Sections 4 and 5 of the report are contained in Part A. The environmental assessment of refineries and the control technology evaluation are presented in Part B. The background information and data necessary for the assessment and evaluation are also included in Part B, which contains Sections 6, 7, and 8 of the report.

Section 4 contains a description of the methodologies used to determine fugitive and process emission rates as well as to characterize fugitive hydrocarbon emissions. The results of the emissions measurements at 13 petroleum refineries are summarized in Section 5. The results of the program and interpretations of the data are presented in this section also.

Section 6 of this report contains a discussion of some potentially hazardous substances which may be present in refinery feed, intermediate, product, and waste streams. The individual refinery process technologies are described and characterized in Section 7. An estimate of emissions is also presented for each of the refinery processes.

An environmental assessment was performed to examine the effects of refinery emissions on the surrounding atmosphere. The results are presented in Section 8 of this document.

The appendices of this report, presented in Volumes 2 - 5, contain more detailed descriptions of the program methodologies, a more comprehensive presentation of results, and more extensive discussions about refinery process technology and control technology.

Appendix A (Volume 2) contains detailed descriptions of the sampling methodology used in the refinery assessment program. Included are descriptions of the experimental program design, the emissions sampling methodologies, and the analytical techniques employed in the field sampling segment of the assessment study. Also described are the techniques used to identify and quantitate individual species present in refinery streams and vapor emissions.

Appendix B (Volume 3) contains a detailed summary of the results obtained while measuring emissions to the atmosphere at 13 petroleum refineries. The data and results from the sampling program are displayed in tables and figures. Emission factors, screening relationships, and correlations are presented. The frequency and distribution of emissions sources in refineries are also included. The effects of valve maintenance operations on the leak rate from valves are described in Appendix B.

The quality assurance program and the statistical analysis of the emissions data are presented in Appendix C (in Volume 4). Quality control procedures for screening, sampling, analyses, species identification, and data validation are described. The various types of quality control data collected during the program are included in Appendix C. The statistical analysis of the data is described, and the accuracy and precision of the various data types are discussed.

The procedures used to develop a detailed environmental assessment of refineries are described in Appendix D (in Volume 4). The large volume of refinery emission rate data generated in the refinery assessment program was used to predict ambient air pollutant levels in the vicinity of a model refinery. The environmental effects and the potential hazard to the public are discussed in detail in Appendix D.

Appendix E (in Volume 4) contains a detailed review and evaluation of pollution control technology. The state-of-the-art of fugitive and process emission controls in refineries are reviewed. Available controls are described. Control technologies used in related industries are examined for potential applicability in the refining industry.

A detailed characterization of refinery technology is presented in Appendix F (Volume 5). Petroleum refineries in the U.S. are classified and characterized. Four types or sets of refinery models which could be used to simulate the entire refining industry are included in this appendix. The characteristics of crude oils, other raw materials, intermediate products, and final products are described. Detailed descriptions of current refinery process technology are included. Atmospheric emissions which result during the operation of each process are estimated and presented in Appendix F.

1.1 Program Objectives

The refinery assessment program had three ultimate objectives, all of which addressed important environmental questions concerning the effect of refineries on air quality: (1) quantification of fugitive hydrocarbon emissions from petroelum refineries, (2) evaluation of existing and developing refinery control technologies, and (3) assessment of the potential impact of atmospheric refinery emissions on the surrounding environment.

Over the three year period, the program evolved to focus on these three objectives. The program originally planned to address objectives (2) and (3). Objective (1) was added after work was initiated. Several factors contributed to the addition of Objective (1).

As the work began, it became evident that fugitive emissions were a large, if not the largest, source of hydrocarbon emissions from refineries. Moreover, quantitative information concerning fugitive emissions from refineries was scarce. Because of these developments, the program was modified to incorporate the measurement and estimation of fugitive hydrocarbon emissions from refineries.

This objective was given further emphasis by the Clean Air Act and its emissions off-set regulations. Compliance with these rules necessitated emission factors for use in off-set calculations.

In meeting Objective 1 Radian conducted a field sampling program to obtain data from a number of U.S. petroleum refineries. When necessary, appropriate sampling and analytical methods were developed and verified.

In order to evaluate existing and developing control technologies (Objective 2), Radian analyzed the data obtained from the program's field sampling program. Information obtained from literature sources also contributed to the data base, as did information from vendors and equipment manufacturers.

Statistical and atmospheric dispersion models were used to meet Objective 3. Emission factors developed from the project's field sampling results were used in these models to assess the environmental impact of petroleum refineries.

1.2 Historical Perspective

Some of the more important studies of refinery emissions prior to the refinery assessment program are described in this section. Also described are the potential impacts of refineries on ambient air quality. Since emissions from storage and loading facilities were not within the scope of the refinery assessment program, studies describing emissions from these sources are not included.

1.2.1 Previous Studies on Refinery Emissions

One of the earliest and most comprehensive studies of refinery emissions was made in a joint (district, state, and federal) project carried out in Los Angeles County in 1955 - 57.[1] Extensive field testing was performed to obtain a data base from which emission factors could be developed. Emission sources considered in this study are listed in Table 1-1.

Although substantial amounts of information were obtained from the Los Angeles Joint Study, data gaps existed. Leak screening methods were sometimes inadequate. Relatively insensitive techniques were sometimes used to measure leak rates. Losses from some unit operations may have been inaccurately estimated.

In 1971, Litchfield published hydrocarbon emission factors for uncovered and covered API separators.[2] The hydrocarbon evaporative losses were determined under laboratory controlled conditions with simulated covered and uncovered API separators. The simulated separator covers consisted of a cellular glass insulation floating directly on the oil. In the laboratory simulation study, Litchfield found that evaporative loss from an uncovered separator varied with ambient temperature, influent

TABLE 1-1. EMISSION SOURCES EXAMINED IN THE LOS ANGELES COUNTY JOINT STUDY

Valves and flanges
Pressure relief valves
Catalytic cracking regenerator stacks
Cooling towers
Compressor seals
Pump seals
Boilers and process heaters
Air blowing operations
Blind changing operations
Loading facilities
Turnarounds, equipment maintenance, and blowdown systems
Wastewater separators and process drains
Gas compressor internal combustion engine exhaust
Waste gas flares
Vacuum jets

Source: Reference 1.

temperature, and the ten percent true boiling point of the oil. However, no attempt was made to verify the laboratory findings with the performance of actual API separators.

In 1976, 19 valves, four compressors, two pumps, and two regulators were tested for hydrocarbon emissions at a California gas plant.[3] The fugitive hydrocarbon emission rate was found to be very low, less than one percent of the rates found in the Joint Study. This small data base, however, was inadequate for making any conclusions regarding the results.

Ambient concentrations and fugitive emission rates from fittings (primarily valves and flanges) in a Colorado natural gas producing field were measured in a 1976 study.[4] No leaking flanges were found, but 16 percent of the tested valves leaked. The valve leak rates varied significantly with time. Only cool valves were included in the study, but this included most of the fittings in the gas field.

The California Air Resources Board (CARB) sponsored a study of all organic species emissions in the South Coast Air Basin.[5,6] Oil refineries, accounting for about ten percent of all organic emissions, were included in the project. Two refineries were visited over a three week period. Fugitive emissions were monitored from 5,800 valves, 12,000 flanges, 115 pumps, five compressors, three cooling towers and three oil/water separators. Soap solution was primarily used to detect and estimate emissions. It was concluded that "the emission factors in AP-42[7] are reasonable estimates for average emissions, and that refinery fugitive emissions are primarily paraffins with low photochemical reactivity." However, economic constraints limited the amount of testing conducted. The emission rates from only 25 valves and 25 pump seals were actually measured. The remaining leak rates were estimated from visual observations or from hydrocarbon detector readings.

In June 1978, EPA's Office of Air Quality Planning and Standards published a guideline report entitled "Control of Volatile Organic Compound Leaks from Petroleum Refinery Equipment."[8] In this document, the frequency of leaks found by EPA in source testing at four refineries was reported. The tested sources included 482 pump seals, 15 compressor seals, 940 block valves, 287 control valves, 43 open-ended lines, 367 drains, and 15 pressure relief devices. The devices were tested by monitoring the hydrocarbon concentration with a portable hydrocarbon detector at a position five centimeters from the emission area. A concentration of 1,000 ppmv or greater was designated a "leak." Thirteen percent of the inspected pump seals, seven percent of the compressor seals and six to seven percent of the valves were found to leak.

In February 1978, members of CARB conducted an inspection of valves and flanges in six refineries in Los Angeles. Sources in 49 process units were inspected. Over thirteen thousand valves and nearly 25,000 flanges were included in the study.[9] Sources were classified as "non-leaking," "slow-leaking," or "fast-leaking" based on visual inspection of soap solution applied to the source. CARB found that approximately nine percent of the inspected valves leaked, and determined an average leak rate of 0.11 lb/day for all of the inspected valves. Apparently, no hot valves ($> \sim 180°F$) were inspected, since hot valves cannot be accurately inspected with soap solution. Error limits or a confidence interval for the emission factor were not reported.

1.2.2 Impact of Refineries on Ambient Air Quality

Petroleum refineries are sources of primary criteria pollutants such as SO_x, CO, NO_x, hydrocarbons, and particulates. A detailed emission estimate for 1976 for major sources of these pollutants is shown in Table 1-2.[10] As the table indicates, emissions from refineries made up from 0.7 percent to 3.2 percent of the total of all criteria pollutants from all sources in the United States. Hydrocarbon emissions from refinery processes

TABLE 1-2. DETAILED ANNUAL EMISSION ESTIMATES - 1976[10]

Pollutant	Transportation Source Emissions		Standard Fuel Combustion Emissions		Industrial Process Petroleum Refinery		Emissions Other Processes		Solid Waste Source Emissions		Miscellaneous Source Emissions	
	10^6 Metric Tons per Year	% of Total U.S. Emissions	10^6 Metric Tons per Year	% of Total U.S. Emissions	10^6 Metric Tons per Year	% of Total U.S. Emissions	10^6 Metric Tons per Year	% of Total U.S. Emissions	10^6 Metric Tons per Year	% of Total U.S. Emissions	10^6 Metric Tons per Year	% of Total U.S. Emissions
Particulates (TSP)	1.2	9.0	4.6	34.3	0.1	0.7	6.2	46.3	0.4	3.0	0.9	6.7
SO_x	0.8	3.0	21.9	81.4	0.7	2.6	3.4	12.6	0.0	0.0	0.1	0.4
NO_x	10.1	43.9	11.8	51.3	0.3	1.3	0.4	1.7	0.1	0.4	0.3	1.4
Hydrocarbons*	10.8	38.7	1.4	5.0	0.9	3.2	8.5	30.5	0.8	2.9	5.5	19.7
CO	69.7	79.9	1.2	1.4	2.4	2.8	5.4	6.2	2.8	3.2	5.7	6.5

*Hydrocarbon emission estimates are basically for total hydrocarbons. Sources that emit only methane are generally not included. Sources that emit a mixture of hydrocarbons, including methane, would include methane in the total hydrocarbon emission estimates.

are approximately 3.2 percent of the total hydrocarbon emissions from all man-made sources in the United States. Hydrocarbon emissions from refinery-associated storage facilities are included in the "Other Process" category of Industrial Process Emissions.

Sittig[11] estimated the emissions from 262 United States refineries (1969) as follows (in 10^6 metric tons/year):

Particulates	0.1
SO_x	2.0
NO_x	0.1
HC	2.1
CO	2.2

Sittig's estimates of SO_x and hydrocarbon emissions from refineries are higher than shown in Table 1-2. However, Sittig's calculations were very general, and he assumed no control of SO_x emissions and 50 percent control of hydrocarbon emissions.

More recently, Wallace[12] estimated hydrocarbon emissions from petroleum processes to be 4.5×10^6 and 4.6×10^6 metric tons per year in 1974 and 1975, respectively. This is much higher than the EPA estimate of 0.9×10^6 metric tons per year for 1976. However, Wallace calculated the emissions using emission factors from AP-42.[7] The emission factors for uncontrolled sources may have been exclusively used. Additionally, hydrocarbon emissions from storage facilities were also apparently included in the total.

The impact of refineries on ambient air quality has been studied both theoretically and experimentally. Several studies of ambient air quality in the vicinity of petroleum refineries have been made. In 1975, the American Petroleum Institute published the results of a study involving refinery odor control and ambient levels of pollutants from refinery operations.[13] As part of this project, the ambient air at five refineries was sampled. The ambient air in nearby residential areas was also sampled. All of the ambient air samples were analyzed for total hydrocarbons (THC), organic sulfur compounds (RSH), NH_3, and SO_2.

Residential and other sites at distances of approximately 1 - 2 miles had ambient air concentrations of pollutants as shown below:

SO_2: 0.00 - 0.04 ppmv
NH_3: 0.01 - 0.02 ppmv
THC: 1.8 - 4.7 ppmv
RSH: 0.00

Background concentrations of these pollutants were in the following ranges:

SO_2: 0.00 - 0.001 ppmv
NH_3: 0.007 - 0.01 ppmv
THC: 0.3 - 0.8 ppmv
RSH: 0.00 ppmv

In another study, Westberg, et al.[14] sampled ambient air for hydrocarbons, CO, NO_x, and ozone downwind of the Texaco refinery in Lawrenceville, Illinois. This particular refinery was selected because it was a large plant located in a region relatively devoid of other industrial and urban emission sources. Westberg found that the refinery plume could be identified on the basis of elevated hydrocarbon levels out to a distance of 25 miles. At a distance of 1.5 miles from the refinery, the plume contained nonmethane hydrocarbon (NMHC) at concentrations of 1 - 2 ppmv, CO levels of 3 - 5 ppmv, NO_x concentrations in the range of 30 ppb. A decrease in the ozone concentration was noted in the plume compared with the ozone levels outside the plume. Background levels of the species outside of the plume were about 0.2 ppm for NMHC, about 0.7 ppm for CO and 15 ppb for NO_x.

Westberg found that most of the hydrocarbons in the plume were alkanes. There was no evidence of ozone formation in the plume as it moved downwind of the refinery. The deficiency of ozone in the plume was attributed to the reaction of ozone with NO_x present in the plume.

In 1975 Sexton and Westberg[15] conducted an ambient air monitoring program to characterize airborne emissions from the Exxon petroleum refinery in Benicia, California. The refinery plume could be tracked up to eight miles downwind of the plant. Sexton and Westberg found elevated levels of total hydrocarbons (THC), nonmethane hydrocarbons (NMHC), CO, and NO_x within the Exxon plume at distances of less than five miles downwind. Elevated NMHC levels persisted as far downwind as eight miles. A typical plume composition at a distance of 1.5 miles downwind of the refinery is shown in Table 1-3. The ambient air composition outside of the plume is also shown. All the measured species, with the exception of ozone, show elevated concentrations in the plume. The concentration of ozone in the plume was substantially below that found in the air outside of the plume. This was attributed to the scavenging action of nitric oxide, the low levels of "reactive" hydrocarbons, and the velocity of the plume. Only about 30 minutes was required for the plume to travel eight miles. Ozone was formed when bag samples of plume air were irradiated in sunlight for six hours.

Studies of refinery siting problems have been made in recent years. In these cases, atmospheric dispersion models are used to predict maximum ambient air pollutant concentrations. These concentrations are then compared to various federal standards as well as state and local ambient air standards.

In 1974, Radian[16] investigated problems associated with siting refineries at five different locations in the United States. Dispersion

TABLE 1-3. TYPICAL PLUME COMPOSITION AT A DISTANCE OF 1.5 MILES DOWNWIND OF EXXON'S REFINERY AT BENICIA, CALIFORNIA[15]

	Concentration of Species in Air, ppmv	
Measured Species	In Plume 500 ft. Above Ground Level	Out of Plume 500 ft. Above Ground Level
CH_4	2.0 ± 0.1	1.7 ± 0.1
Total Hydrocarbon	2.3 ± 0.1	1.7 ± 0.1
Nonmethane Hydrocarbon	0.3 ± 0.1	< 0.1 ± 0.1
CO	0.7 ± 0.1	0.4 ± 0.1
NO_x	0.07 ± 0.005	0.02 ± 0.005
O_3	0.03 ± 0.005	0.06 ± 0.05

models were used to predict ambient air quality in the vicinity of hypothetical refineries. The size of the hypothetical refineries varied from 180,000 to 250,000 barrels per day. This study found that the predicted maximum ground level concentrations of SO_2, NO_x, particulates, and CO from refinery operations did not exceed the federal primary and secondary ambient air quality standards at any of the sites. However, the predicted hydrocarbon concentration exceeded the existing federal guidelines at all sites by a factor ranging from 20 - 40.

In a similar study, Cavanaugh, et al.,[17] performed dispersion modeling of a model 300,000 barrel per day refinery sited in Brazoria, Texas. The results of the modeling are shown in Table 1-4. It can be seen that the predictions indicate the ambient air levels of SO_2, particulates, NO_x and CO are well below federal ambient air quality standards. However, the predicted hydrocarbon concentration exceeded the federal guidelines for three-hour maximum (6 - 9 AM) nonmethane hydrocarbons concentration of 160 $\mu g/m^3$ (0.24 ppmv). Nonmethane hydrocarbon concentrations of 20 - 40 times the guideline concentrations were predicted in the ambient air in the vicinity of the refinery. It should be noted that this federal guideline is no longer widely accepted or used because the relationship between ozone formation and ambient hydrocarbon concentrations is not adequately defined.

TABLE 1-4. SUMMARY OF FEDERAL AMBIENT AIR QUALITY STANDARDS AND PREDICTED MAXIMUM CONCENTRATIONS FOR 300,000 BPCD REFINERY EMISSIONS

(Units are Micrograms per Cubic Meter with Parts per Million in Parentheses)

	Federal Primary Standard	Federal Secondary Standard	Computed Maximum[a] Annual Average	Computed Maximum[a] 24 hr Average	Computed Short-Term Maximum[a] Unstable Condition	Computed Short-Term Maximum[a] Stable Condition	Computed Short-Term Maximum[a] Typical Conditions
Sulfur oxides		-		-	-	-	-
Annual average[b]	80(0.03)	-	4.2(0.002)	-	-	-	-
24 hr maximum[c]	365(0.14)	-	-	26.5(0.01)	-	-	-
3 hr maximum[c]	-	1,300(0.5)	-	-	135(0.051)	> 36[d]	36.1(0.014)
Particulate							
Annual average[e]	75	60	0.7	-	-	-	-
24 hr maximum[c]	260	150	-	5.1	-	-	-
Nitrogen dioxide							
Annual average[b]	100(0.05)	-	5.3(0.003)	-	-	-	-
Nonmethane hydrocarbons							
3 hr maximum[c], 6 to 9 AM	160(0.24)[f]	-	-	-	1,500(2.26)	40,000(60.26)	605(0.01)
Carbon monoxide							
8 hr maximum[c]	10,000(9)	-	-	-	9.6(0.01)	-	-
1 hr maximum[c]	40,000(35)	-	-	-	14.6(0.01)	-	4.4(0.004)

[a] Maximum values are those that occur on or outside the plant boundary.

[b] Arithmetic mean.

[c] Not to be exceeded more than once per year.

[d] This maximum is beyond the computational range used.

[e] Geometric mean.

[f] This standard is interpreted by EPA to be a guideline and not a regulation.

2.0 CONCLUSIONS

Several important conclusions can be drawn from the results generated by this work. Conclusions and significant results which support them are highlighted in this section. A more complete summary of the results of this program is included in Section 5. For convenience, the conclusions are presented in sections which correspond to the three major objectives presented in Section 1. Section 2.1 contains important conclusions concerning fugitive emissions. Control technology evaluations are presented in Section 2.2. Section 2.3 presents conclusions derived from analysis of the environmental impact of refineries on their surrounding areas.

2.1 Fugitive Emissions

Fugitive emissions are generally characterized by a diffuse release of vaporized hydrocarbon or other organic compounds. They originate from equipment leaks as well as large and/or diffuse sources. In this study, fugitive emission sources are categorized as either "baggable" sources or "nonbaggable" sources.

Baggable sources are those that can be enclosed in some type of "bag" or "tent" to measure their emission rates. Source types included in the baggable category include valves, flanges, pump seals, compressor seals, drains, and relief valves.

Nonbaggable sources of fugitive emissions are those sources which are too large or diffuse to enclose. Emission estimates must be made by indirect means. Nonbaggable sources include cooling towers, wastewater treating units, spills, turnarounds, blind changing, coking, air blowing, vacuum jets, barometric condensers, and sampling operations. Only cooling towers, oil-water separators, and dissolved air flotation units were actually sampled in this study. Information was obtained by survey forms about maintenance practices, turnarounds, blind changing, and sampling operations.

Five major conclusions may be drawn about fugitive emissions in refineries. These conclusions are presented below. They are followed by significant results which support them. Supporting data are organized by source type.

2.1.1 Major Conclusions

Substantial hydrocarbon emissions occur from fugitive sources in refineries.

The estimated nonmethane hydrocarbon emissions from eight sources in the process units of a hypothetical* 330,000 BPD refinery are about 630 pounds per hour (approximately 2,600 tons per year). The emissions and their sources are shown in Table 2-1. The hypothetical refinery was assumed to have covered API separators.

Hydrocarbon emissions from process sources (stacks) are minimal. An FCCU unit equipped with a CO boiler emits from 1 to 12 pounds of nonmethane hydrocarbons per 1,000 barrels of feed. This is equivalent to 2 to 25 pounds per hour of emitted hydrocarbons.

The only equipment or process variable found to correlate with fugitive emission rates was the volatility and/or the phase of the process stream.

The various source leak rates were correlated with all available process and equipment variables. The volatility range and/or phase of the

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*Arthur D. Little Gulf Coast Cluster Model Refinery - Capacity 330,000 BPD.[137]

TABLE 2-1. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM SOURCES IN PROCESS UNITS OF A HYPOTHETICAL 330,000 BPD REFINERY

Fugitive Source	Nonmethane Hydrocarbon Emission Rates lb/hr	Nonmethane Hydrocarbon Emission Rates Tons/year[a]
Valves	305	1,270
Flanges	25	104
Pump Seals	60	250
Compressor Seals	29	121
Drains	48	200
Vessel Relief Valves (gas)	21	87
API Separators (from AP-42[7])[b]	138	574
Cooling Towers	2[c]	8
	628	2,614

[a] Assuming 95 percent on-stream time for process units.

[b] Separators are covered.

[c] Controlled emissions.

process stream correlated with the log of the leak rates with simple correlation coefficients of 0.65 to 0.75. Correlation coefficients between log leak rate and other tested variables ranged between 0.01 and 0.35, indicating very low degrees of correlation.

Valves were found to be the largest contributors of fugitive emissions from baggable source types.

For a 330,000 BPD hypothetical refinery, valves were estimated to emit approximately 300 pounds of nonmethane hydrocarbons per hour. The total hydrocarbon emissions from fugitive sources in this refinery was estimated to be about 630 pounds per hour. Thus, valves are responsible for about 50 to 60 percent of the fugitive hydrocarbon emissions. The hypothetical refinery was assumed to have covered oil-water separators.

The major portion of fugitive emissions from any baggable source type come from a small fraction of the sources.

For example, approximately 70 percent of the nonmethane hydrocarbon emissions from valves in gas service come from only one percent of the valves in that service. In this study, approximately 5,700 baggable sources were screened and about 1,300 were sampled. Sixty-five percent of the total measured emissions came from one percent of the baggable sources.

It is possible to estimate fugitive emission rates from individual sources using portable hydrocarbon detectors as monitoring devices.

It was found that the measured leak rate from a baggable source could be correlated with the hydrocarbon concentration very near the leak. This hydrocarbon concentration (or "screening value") was measured with sensitive portable hydrocarbon detectors. The screening values correlated quite highly with leak rates. A correlation coefficient of 0.72 was obtained for the screening values and the leak rates of valves. The correlation coefficients for leak rates and screening values for all sources ranged between 0.67 and 0.79.

2.1.2 Significant Supporting Results

Some of the significant results of this study which support the conclusions presented in the previous Section 2.1.1 are presented below. The results are given for each source type.

2.1.2.1 Baggable Sources

Valves

(a) Valve emissions from a 330,000 BPD hypothetical refinery were estimated using valve counts and valve emission factors. Approximately 300 pounds per hour of nonmethane hydrocarbons or 64 percent of the emissions from the six baggable source types were emitted from leaking valves.

(b) Valves in gas service have higher emission rates compared to valves in light liquid and heavy liquid service. The emission factor for valves in gas service is 0.059 lb/hr-source. In comparison, valves in light liquid and heavy liquid service have emission factors of 0.024 and 0.0005 lb/hr-source, respectively.

(c) The parameter which has the most influence on valve emissions is the stream type (gas, light liquid/two-phase, or heavy liquid). All other parameters which were evaluated had little or no influence on the emission rate from valves.

(d) The majority of emissions come from a small fraction of valves which leak at relatively high rates. For example, approximately 75 percent of the emissions from valves in light liquid service come from 10 percent of the valves in that service.

(e) Valve leaks of hydrocarbons can be detected with portable hydrocarbon detectors. These instruments must be used at or very near the individual leak sources. Leak rates as low as 0.00001 lb/hr were detected with these devices.

(f) The leak rate of hydrocarbons from valves can be correlated with the concentration of hydrocarbons at the source as determined with a portable hydrocarbon detector. Nomographs showing this relationship have been developed. (See Section 5 of this report.)

Pump Seals

(a) Pump seals are the second largest source of emissions from baggable sources in refinery process units. In a 330,000 BPD hypothetical refinery, pump seals were estimated to emit 56 pounds per hour, or 12 percent of the total nonmethane hydrocarbon emissions from the baggable sources.

(b) Pump seals in heavy liquid (kerosene and higher-boiling) streams leak substantially less than those in light liquid (boiling below kerosene) service. The emission factors are 0.25 lb/hr-source for pump seals in light liquid service and 0.046 lb/hr-source in heavy liquid service.

(c) Variables and parameters other than stream type did not correlate to any significant degree with the seal leak rates. Correlations were attempted but correlation coefficients ranged from 0.01 to 0.24.

(d) Pump seal leaks could be adequately detected with a portable hydrocarbon detector. Leak rates as low as 0.00001 lb/hr were detected and measured.

(e) The leak rates from pump seals can be expressed as a function of the hydrocarbon concentration (screening value) at or very near the leak site. Nomographs illustrating this relationship have been developed. (See Section 5 of this report.)

(f) The major portion of the pump seal emissions are emitted from a small fraction of the seals. For example, 95 percent of the total emissions from the pump seals in light liquid (liquids boiling below kerosene) service come from 20 percent of the seals.

Compressor Seals

(a) Seals on compressors handling hydrocarbon gas streams have the highest emission factor of any baggable source. This emission factor is 1.4 lb/hr-source.

(b) Compressor seal leaks can be detected with a portable hydrocarbon detector. Leak rates as low as 0.001 lb/hr have been detected.

(c) The emission rate from compressor seals can be correlated with the hydrocarbon concentration as determined with a portable hydrocarbon detector at or very near the leak site. A correlation coefficient of 0.68 was determined for this relationship.

(d) Compressor seals leaked with a frequency higher than that of any other baggable source. Seventy-seven percent of the screened compressor seals had screening values $\geqslant$ 200 ppmv.

(e) The bulk of the emissions from compressor seals are released from a minority of the seals. Seventy-one percent of the total compressor seal emissions were emitted from 13 percent of the screened seals.

Flanges

(a) Flanges have a very low frequency of leakage. Less than three percent of the screened flanges had screening values $\geqslant$ 200 ppmv.

(b) Flanges leak at very low rates. They have the lowest emission factor of the six baggable source types, 0.00056 lb/hr-source.

(c) Hydrocarbon leaks from flanges can be detected with portable hydrocarbon detectors. Leak rates as low as 0.00001 lb/hr have been detected.

(d) The hydrocarbon leak rate from flanges can be estimated from the hydrocarbon concentration at or very near the leak point. The correlation of leak rate with screening values has a correlation coefficient of 0.77.

(e) The leak rate of flanges is a statistically significant but weak function of the diameter of the flange. The leak rate increases slightly with increasing diameter. The pressure or temperature of the process fluid did not influence the leak rate from flanges.

Drains

(a) The frequency of emitting process drains is relatively low. Only 19 percent of the inspected drains had screening values ⩾ 200 ppmv.

(b) Hydrocarbon emissions from drains can be detected with portable hydrocarbon detectors. Leak rates of 0.0001 lb/hr were detected.

(c) The hydrocarbon emission rate from drains can be estimated from the hydrocarbon concentration at or very near the emission point. A correlation coefficient of 0.68 was observed for this correlation.

(d) Most of the hydrocarbon emissions come from a small fraction of drains. For example, fewer than six percent of the screened drains were responsible for 95 percent of the total drain emissions.

Relief Valves

(a) Portable hydrocarbon detectors are effective for detecting emissions to the atmosphere from pressure relief valves. Very low leak rates (< 0.0001 lb/hr) can be detected.

(b) A substantial majority of the hydrocarbon emissions from pressure relief valves come from a small fraction of the relief valve population. For example, 76 percent of the hydrocarbon emissions from relief valves are emitted from just three percent of the sources.

(c) It is possible to estimate the fugitive hydrocarbon emission rate from the hydrocarbon concentration at the outlet of pressure relief valves. A correlation coefficient of 0.68 was found for this relationship.

2.1.2.2 Nonbaggable Sources

Sampled nonbaggable emission sources include cooling towers and units of the wastewater treating system.

Cooling Towers

(a) The majority of cooling towers in refineries do not emit significant quantities of hydrocarbons. Only eight of the 31 sampled towers, or 26 percent, had statistically significant emissions.

(b) The concentration of volatile organic compounds in the cooling tower streams were most precisely determined with a purging technique developed for this purpose.

(c) Thirty-one cooling towers were tested for hydrocarbon emissions using two different analytical techniques. One method (purge method) was found to be significantly more precise than the other procedure (total organic carbon analysis). Therefore, an emission factor of 0.00011 pound per 1,000 gallons of cooling water was developed using only the purge method data from the fifteen towers analyzed with this method. A 95 percent confidence interval for this factor ranges from negligible to 0.0004 pounds per 1,000 gallons of cooling water.

Wastewater Treatment System

(a) Intermittent sampling and subsequent analyses of oil-water separator liquids did not provide an adequate technique for accurately estimating hydrocarbon emissions from these devices.

(b) It is difficult, if not impossible to make an accurate hydrocarbon material balance around oil-water separators. The rate and composition of the incoming liquid stream are continually changing.

(c) Hydrocarbon emissions from dissolved air flotation units were estimated from a material balance using measurements of volatile hydrocarbons in the inlet and outlet water streams. However, the data were insufficient to allow the development of an emission factor which could be used with confidence.

2.1.2.3 Miscellaneous Refinery Practices

The emission potential of a number of refinery practices were evaluated from survey forms and discussions with refinery personnel. No attempt has been made to quantitate emissions from these activities. Results of the survey of these current practices are presented below:

Turnaround and Blind Changing

(a) Data on emissions during turnarounds could not be developed during this study. However, it is felt that the overall impact of turnarounds on fugitive hydrocarbon emissions is small if the units are adequately purged prior to opening the process vessels. Typical industry practice provides venting of hydrocarbons and purge gases to flares or vapor recovery systems.

(b) Other emission sources during turnarounds include steaming of heat exchanger bundles, draining of pumps, emissions during startup, etc. However, turnarounds in refinery units are generally infrequent, so total emissions from these sources are felt to be small.

(c) Refineries generally do not routinely change significant numbers of pipeline blinds. Most blind changing takes place during the startup or shutdown of a unit.

2.2 Control Technology

As part of this study, pollution control technology for refinery emission sources was reviewed and evaluated. Research and development needs were also evaluated. The major conclusions reached in control technology evaluation are organized in three parts: 2.2.1 Hydrocarbon Emission Controls, 2.2.2 Stack and Process Emission Controls, and 2.2.3 Research and Development Needs.

2.2.1 Fugitive Hydrocarbon Emission Controls

Effective control methods are available for the majority of hydrocarbon Emission sources in refineries. Although these methods are being currently used in some refineries, they may not be universally applied. Safety and economic factors may deter their use in some refineries. Comments on control techniques for fugitive hydrocarbon emissions are included below by source type.

2.2.1.1 Valves

The existing method of controlling fugitive emissions from valves and pump seals is based upon visual detection of leaks. This method allows numerous and substantial leaks to go undetected. However, this study determined that simple valve monitoring and maintenance programs employing portable hydrocarbon detectors are effective in reducing fugitive emissions from valves. Such programs can reduce average valve emissions by 50 to 90 percent for the maintained sources.

Packless valves have been suggested as alternatives to valves in current use. These valves (diaphragm and bellows valves) are currently available. However, their performance characteristics, size limitations, and cost may preclude wide-spread use in refineries. However, their utility and usefulness in refinery application has not apparently been widely tested.

2.2.1.2 Pumps

As mentioned above in the discussion of valve controls, the present visual inspection technique is inadequate for control of fugitive emissions. It has been established that portable hydrocarbon monitoring equipment is effective in locating pump seal leaks. However, no study has been made of the emission reductions effected by replacing leaking mechanical seals or tightening packed seals.

Hermetically-sealed pumps would virtually eliminate emissions from pump seals. However, these pumps currently have serious limitations for general refinery use. These limitations include efficiency, initial cost, pump life, capacity, head, and maintenance cost.

2.2.1.3 Compressors

Many compressor seal areas are enclosed and vented to a blowdown flare system. This is an effective means for reducing emissions to the atmosphere.

Portable hydrocarbon detectors can be used to detect emissions from compressor seals and seal enclosures. A program of seal monitoring (with hydrocarbon detectors) and subsequent maintenance of leaking seals may further reduce compressor seal emissions. Such a potential reduction, however, has not been experimentally determined or quantified.

2.2.1.4 Safety Relief Valves

A significant fraction of safety relief valves in refineries discharge to blowdown/flare systems. Atmospheric emissions from these systems should be small if the flare system is operating effectively. Leaks were found in approximately 40 percent of the relief valves discharging to the atmosphere instead of blowdown systems. In some refineries, pressure relief valves are inspected regularly, but these inspections are apparently not completely effective in minimizing hydrocarbon emissions. Rupture disks can be used in series with safety relief valves to reduce emissions to the atmosphere. The combination may, however, present safety problems in some applications. A pressure or flow sensor could be installed between the relief valve and the rupture disk as a safety precaution.

2.2.1.5 Flanges

The leak frequency and emission rates of flanges are low. Refineries currently depend on visual inspection to detect leaks. The flange installation and inspection procedures are apparently adequate for maintaining a low level of emissions. Flanges may be less prone to developing leaks after installation since there are no moving parts.

2.2.1.6 Process Drains

The majority of process drains in refineries are uncovered, and a substantial fraction are also untrapped. Emissions are significant in quantity. Process drains could be trapped and covered (at least partially), if safe operating conditions can be maintained. The buildup of explosive vapors in such systems is a potential safety hazard that must be considered. It should also be noted that the effectiveness of traps and covers for reducing emissions has not been evaluated.

2.2.1.7 API Separators

Many API separators in refineries do not have covers. These devices are assumed to emit significant quantities of hydrocarbons to the atmosphere. Corrugated-plate interceptors (CPI) and parallel-plate interceptors (PPI) are used in some refinery applications to separate oil and water. These devices generally allow very little exposure of oil to the atmosphere. In fact, they are often completely covered.

According to AP-42,[7] covered API separators emit smaller amounts of hydrocarbons to the atmosphere than uncovered units. The data obtained in field measurements around both covered and uncovered oil-water separators were inadequate for defining emission rates. The AP-42[7] emission factors are given a quality rating of "D." Emission factors of this quality are considered "below average," i.e., there is not very much measured emission data, process data, or engineering analysis upon which to base the factor. Additional studies and data are needed to provide better estimates of control effectiveness.

2.2.1.8 Cooling Water

In many refineries cooling tower water is periodically monitored for hydrocarbon content. Frequent monitoring will provide prompt indication of leakage of hydrocarbons into the cooling water (with subsequent emission to the atmosphere). This procedure, followed up with maintenance to repair the leak, appears to be quite effective in maintaining a low emission level.

2.2.2 Stack and Process Emission Controls

Although hydrocarbon emissions from these sources are low, other criteria pollutant emissions may be significant. Of the criteria pollutants, sulfur oxide emissions from stacks in refineries are a difficult control problem. Although adequate controls may be available, they can be very expensive and in some instances may present safety problems. Furthermore, the decreased availability of low-sulfur crude oil and natural gas and the increased use of heavier oils as fuel for refinery boilers and heaters will result in higher emissions from these sources.

Claus plants are the accepted method for recovering sulfur in refineries. The tail gas from Claus units contains substantial quantities of SO_x and H_2S. There are a number of Claus tail gas treatment processes which are capable of reducing the SO_x content of tail gas to 250 ppmv or less. Some of these are currently in use in refineries. In the absence of tail gas treating, the gas is incinerated to remove H_2S.

No pollution control devices are currently in use to treat the flue gases from refinery boilers and process heaters. When low SO_x and NO_x emissions are required, low sulfur fuels and high efficiency burners are used. Flue gas desulfurization (FGD) processes for removing SO_x from combustion gases have been developed for the electric power industry. These are potentially applicable to heater/boiler flue gases. Most of the numerous individual combustion sources found in refineries are relatively small, however. The flue gas from several sources would have to be combined before scrubbing. This is very costly and could present safety problems. Additionally, large amounts of scrubber waste could produce disposal problems.

The emissions of sulfur oxides from fluid catalytic cracking unit (FCCU) regenerators can be reduced. The available methods are, however, expensive and in some cases have not been commercially proven.

Amoco Oil Company (as well as other oil companies and catalyst manufacturers) has developed an FCC catalyst which reportedly reduces the amount of SO_x leaving the regenerator in the flue gas.[18] This catalyst appears to be a promising alternative to other potential control methods such as flue gas scrubbing or feedstock desulfurization. Results of commercial scale testing of the Amoco catalyst or those of other developers has not been reported.

Scrubbing of FCCU flue gas for the removal of SO_x is currently practiced in only a few refineries. These scrubbers are reportedly capable of removing up to 95 percent of the SO_x in the flue gas.[19]

The hydrodesulfurization (HDS) of FCCU feedstock can also result in the reduction of SO_x in the regenerator flue gas. HDS is generally not practiced for emission control purposes, but rather to increase the volume and/or quality of saleable products. The installation of a large hydrodesulfurization unit is quite costly, and may also require the addition of a hydrogen unit.

2.3 Environmental Impact

An environmental assessment was performed to examine the potential effects of refinery emissions on the surrounding atmosphere. The primary objective of this assessment is to provide guidance in identifying potential problem areas. For instance, it can provide insight into which sources and which pollutants appear to be the most likely to pose potential hazards, if such hazards exist. The approach taken in this study to an environmental assessment of a generalized source (model refinery) is of limited value in providing specific information on whether steps need to be taken to further reduce emissions of a given pollutant. As a result, this type of environmental assessment is only a tool to aid in the evaluation of relative potential environmental impacts. It is not a method for making precise and accurate predictions of such impacts. The results should not be regarded as an absolute value which can be used to predict violations of standards, public health hazards, requirements for additional pollution control technology or regulatory requirements.

In this assessment, an atmospheric dispersion model was used to estimate the impact of a large model refinery on the ambient air quality in the surrounding area. The refinery configuration emission rates, meteorological conditions, dispersion model, etc., are consistent with a "worst case" study. Worst case conditions were chosen to permit some generalization of the results of the refinery assessment. If the worst case analysis shows little or no impact, then it can be said with some confidence that refineries in general have little or no impact.

The EPA guideline dispersion model RAM (rural version) was used in this assessment. None of the available models is perfect, and predicted maximum concentrations may vary from half to ten times (or more) the actual concentrations measured from a source. In addition, the use of the rural version of RAM to model a refinery is a conservative (or worst case) choice. In the rural version, the heat island effect of the refinery, which would tend to increase atmospheric diffusion, is not considered. These factors should be considered when interpreting the results of this study.

Emissions from storage tanks were not included in the scope of this study, and they were not considered in the dispersion model. However, the magnitude of these emissions were estimated to provide a basis of comparison to other hydrocarbon emission sources.

The dispersion modeling results indicate that in the worst case situation, hydrocarbon emissions were the only potentially significant environmental pollutant. Ambient levels of particulate matter, sulfur oxides, nitrogen oxides, and carbon monoxide were all predicted to be well below the National Ambient Air Quality Standards (NAAQS).

Total nonmethane hydrocarbon concentrations in excess of the federal guidelines were predicted in an area which extended 3.5 kilometers downwind of the model refinery and encompassed about four square kilometers. The maximum total hydrocarbon concentration was estimated to be directly downwind of a covered API separator. The bulk of the hydrocarbons appeared to be from the alkane family. However, both the aromatic and polynuclear aromatic (PNA) species were estimated to be present at the part-per-billion level. Maximum concentrations of benzene, naphthalene, anthracene, biphenyl, and other PNA's were predicted to be located adjacent to and downwind of the covered API separator.

Several factors should be kept in mind, however, when considering the results concerning the API separators:

- The separator was located right on the plant boundary. This placement is quite unusual.
- There is a great deal of uncertainty in the emission factor for separators. No conclusive results were obtained from limited testing of separators in this study. As a result, factors from AP-42[7] were used in this environmental analysis.

- The emissions from an API separator are highly variable in component breakdown. The species concentrations were based on grab samples of surface oil. These samples may not have been reflective of "typical" operations.

Another point of uncertainty is the potential contribution of storage emissions to the impacts predicted for the refinery process area. Storage emissions were estimated and storage modules were located in the refinery plot plan. It was determined that the inclusion of storage emissions in the dispersion modeling would probably not have significantly increased the estimated maximum hydrocarbon concentration in the vicinity of the model refinery. It would, however, have increased the area of impact in which relatively high concentrations of nonmethane hydrocarbons would be predicted by the model.

3.0 AVAILABLE CONTROL TECHNOLOGY OPTIONS

In this section, existing and available control options are discussed. Research and development programs for some specific controls needs are also recommended. These recommendations are Radian's and do not necessarily reflect the positions or policies of the U.S. Environmental Protection Agency (EPA).

3.1 Control Technology for Fugitive Emission Sources

Control technology for baggable and nonbaggable fugitive emission sources are reviewed in detail in Appendix E (Volume 4). All of the available technologies are discussed in Appendix E. The available control options are listed below.

3.1.1 Baggable Sources

3.1.1.1 In-Line Valves

Control Options--The following options are available for the control of hydrocarbon emissions from in-line block and control valves.

(a) Monitoring with portable hydrocarbon detectors of all accessible valves in gas and light liquid service is recommended. The monitoring should be done at regular intervals.

(b) Simple maintenance (tightening packing glands, injection of grease) should be performed on all accessible valves with screening (monitoring) values above some specified level. The maintenance should be performed within a short interval of time after screening.

(c) A portable hydrocarbon detector should be used to guide the maintenance effort. This assures that the maintenance effort will be continued until the leak is minimized.

(d) On-line valve maintenenace can also be achieved by drilling and injection of a sealing compound into the packing area.

(e) Valves that cannot be maintained or repaired while in service should be identified and repaired during the next process unit shutdown and/or turnaround. Packing replacement or valve replacement are feasible during shutdowns/turnarounds (or whenever the valve in question can be isolated).

(f) Monitoring of valves in heavy liquid service is not recommended. Visual inspection should be adequate for detecting leaks. Visible leaks should be repaired.

Research and Development Recommendations--More effective methods of controlling emissions from valves might possibly be developed. Additionally, more data are needed regarding the effectiveness of existing/recommended controls. The studies listed below should be considered:

(a) A study of the effect of deeper stuffing boxes on the leak frequency and emission rates of smaller valves.

(b) A study to define the theoretical and practical limitations involved in developing and applying diaphragm and bellows sealed valves for some refinery services.

(c) A study to define the effectiveness, reliability, and limitations of on-line leak-sealing methods such as sealant injection.

(d) A study of the short-term and long-term effectiveness of valve maintenance. Results from refineries which institute a monitoring/maintenance program would enhance such a study.

3.1.1.2 Open-Ended Valves

Emissions to the atmosphere from open-ended valves (sampling valves, drain valves) occur through the valve seat.

Control Options--Available control options for open-ended valves, are listed below.

(a) The open-end of the line should be closed when not in use. This can be done by installing caps, plugs, blinds, or a second valve on the open-end.

(b) The closures on open-ended valves in gas and light liquid service should be monitored with hydrocarbon detectors at regular intervals to ensure the continuing effectiveness of the device.

3.1.1.3 Flanges

The leak frequency and emission factor for flanges are both very low. Existing methods of flange installation and testing coupled with visual inspection appear to be effective in minimizing emissions of nonmethane hydrocarbons. Periodic monitoring of flanges for leaks is not recommended because of the high cost and minimal expected emission reduction.

3.1.1.4 Pump Seals

Control Options--Pump seals are an integral component of pumps and are necessary for pump operation. There are a number of types and configurations of pump seals. Some types are better suited than others for reducing emissions in certain applications. In addition to the two most commonly used types, packed seals and single mechanical seals, the following options are available:

(a) Double mechanical seals.

(b) Tandem mechanical seals.

(c) Double mechanical or tandem seals with barrier fluid reservoir degassing vent connected to a closed vent system.

(d) Periodic monitoring (with hydrocarbon detectors) and repair (tightening of packing gland, replacement of packing, replacement of seal, etc.).

(e) Pump replacement.

The data from this study are insufficient to determine the relative effectiveness of the above options for controlling pump seal emissions. The utility of any of these options depends to a great degree on the application. The economics, safety, and effectiveness of each control option must be determined for each particular case.

Research and Development Needs--Hermetically sealed or "canned" pumps should achieve complete control of emissions. At the present time they are used sparingly in refineries because of efficiency, pump life, cost, capacity, and head limitations. A study of these pumps is recommended. The study would define the probabilities and costs of overcoming some or all of the current limitations for refinery use.

3.1.1.5 Compressor Seals

Control Options--Compressor seals are an integral component of compressors, and they are necessary for proper compressor operation. Methods for controlling nonmethane hydrocarbon emissions from compressor seals are available for some applications. Those identified below are not the only available options, however. Compressor seals are often engineered on an individual basis. Economic, operational, and safety problems associated with available control options must be evaluated for each installation.

(a) Some compressor seals include a barrier fluid (seal oil) which circulates through the seal area (similar to double mechanical pump seals). The fluid absorbs the compressed gas. Where practical, this fluid can be circulated to a reservoir equipped with a closed degassing vent system. The vent system can be routed back to the compressor intake or be connected to a control device such as a vapor recovery system, flare, or a combustion/incineration device. These seal vent systems are complex and expensive. The cost effectiveness, operating problems, and safety concerns must be evaluated for individual cases.

(b) Some compressor seals, particularly those of reciprocating compressors, are not equipped with seal oil systems. In these cases the seal area can be enclosed, if safety problems are not encountered. The enclosed area should be vented to a closed vent system which is equipped with a vapor recovery or incineration/combustion system.

(c) If it is not feasible to apply the above systems or comparable emission controls to a compressor seal, then regular monitoring of that seal with a hydrocarbon detector is recommended. When significant emissions are detected, the seal can be repaired or replaced at the next opportunity such as a shutdown or turnaround.

3.1.1.6 Safety Relief Valves

Safety relief valves which vent into a blowdown/flare system are effective in limiting hydrocarbon emissions to the atmosphere.

Control Options--The control options given below apply to those safety relief valves in hydrocarbon gas service which vent directly to the atmosphere.

(a) Rupture disks upstream of safety relief valves can be used to reduce emissions to the atmosphere.

(b) Where rupture disks are installed, bubblers, pressure gauges, and/or excess flow valves should be installed between the rupture disk and the safety relief valve. Such an arrangement is covered by ASME code. Leaks through the rupture disks can be detected by the above devices.

(c) Safety or other considerations may preclude the installation of rupture disks upstream of safety relief valves. Those relief valves not equipped with rupture disks should be regularly monitored for hydrocarbon emissions.

(d) In addition to regularly scheduled monitoring, pressure relief valves should be monitored after every pressure release.

Research and Development Needs--There appear to be divergent opinions concerning the practicality, safety, and costs of the universal application of (a) the venting of relief valves to blowdown/flare systems and (b) rupture disks upstream of pressure relief valves. A comprehensive and objective study is recommended to define the costs and safety problems associated with these control measures.

3.1.1.7 Process Drains

Many drains in refineries are used to frequently or continuously carry away liquids such as condensate, oily water, and/or hydrocarbon liquids. Many of these streams are hot and/or volatile. Emissions from the open process drains are not insignificant.

Control Option--Unless prevented by safety or economic factors the covering of existing open process drains is recommended. New process drains should be equipped with traps and covers.

Research and Development Needs--A study is recommended to evaluate the cost, cost effectiveness, and hazard potential of process drain emission control methods.

3.1.1.8 Sampling Systems

When taking samples of refinery process fluids, it is necessary to purge the sampling line of fluid present from the previous sampling. If this fluid is purged into the air (gas) or into drain systems (or onto the ground), atmospheric emissions will result. A closed sampling loop is recommended for sampling operations. A closed sampling loop allows the purged material to flow back into the process line without being exposed to the atmosphere.

3.1.2 Nonbaggable Sources

Nonbaggable sources include cooling towers and units of the wastewater collection and treatment system.

3.1.2.1 Cooling Towers

Cooling towers can emit hydrocarbons to the atmosphere if the cooling water contains hydrocarbons from leaking process heat exchangers.

Control Options--Cooling tower water can be routinely monitored for hydrocarbon content. This is an effective method for detecting the presence of hydrocarbons resulting from leaks. It is recommended as the most effective means for early detection of leaking heat exchangers. Prompt repair of such exchangers will minimize hydrocarbon losses to the atmosphere.

3.1.2.2 Oil-Water Separators

Liquid hydrocarbon wastes are separated from refinery wastewater in oil-water separators. A considerable amount of the hydrocarbon wastes make their way to the oil-water separators, and these units can be very substantial hydrocarbon emission sources if they receive volatile material.

Control Option--The most commonly used control option for reducing hydrocarbon emissions from those oil-water separators receiving volatile material is to cover part or all of the separators. Adequate data are not available for a definitive evaluation of the effectiveness of covers on oil-water separators for reducing atmospheric emissions. It seems reasonable to presume that covers will reduce emissions to some degree. The cost-effectiveness of this control option can only be determined after its control efficiency has been defined through testing. There can be safety and operational problems associated with covering the separators. These must be evaluated on an individual basis.

Research and Development Needs--The Environmental Protection Agency is now conducting a program to measure atmospheric emissions from refinery wastewater treatment units. In addition two topics should be fully explored:

(a) The venting of covered separators to flare systems should be investigated. Such a system might substantially reduce emissions from unvented covered separators.

(b) Corrugated plate interceptors (CPI) and parallel plate interceptors (PPI) are not widely or universally used in refineries. The range of applicability, efficiency, limitations, and economics of operation should be comprehensively explored. If there are serious limitations for refinery service, an R&D program to overcome them may be justified.

3.1.2.3 Wastewater Collection System

Included in this system are drains, process sewers, storm sewers, and ditches.

Control Options--The methods for controlling emissions from the wastewater collection system include:

(a) Drains and sewers can be sealed or vented through liquid seals if safe operating conditions can be maintained. The buildup of explosive vapors in such systems is a potential safety hazard that must be considered.

(b) Pump bases should be constructed or modified to allow rapid and complete drainage to the sewer.

(c) Process water should be segregated from storm water.

3.2 Control Technology for Process Emissions

The major sources of atmospheric process emissions are sulfur recovery processes, fluid catalytic cracking (FCCU) catalyst regeneration, and process heaters and boilers. The major types of atmospheric process emissions from refineries are hydrocarbons, sulfur oxides (SO_x), particulates, carbon monoxide (CO), and nitrogen oxides (NO_x). Process emission controls for the various pollutant types are discussed below.

3.2.1 Control of Hydrocarbon (Including Aldehydes) Emissions

Potential major sources of hydrocarbon emissions include FCCU catalyst regeneration, delayed coking, fluid coking, vacuum distillation, and air blowing operations. Most of these sources are effectively controlled in existing refineries.

3.2.1.1 Fluid Catalytic Cracking Unit (FCCU)

Control Options--Two methods for controlling CO emissions are also effective in reducing hydrocarbons in the flue gas. The following controls are recommended for controlling hydrocarbon emissions.

(a) Carbon monoxide can be further oxidized to CO_2 in a CO boiler. This combustion effectively reduces hydrocarbon emissions to low levels.

(b) High temperature regeneration and combustion promoters also significantly reduce hydrocarbon emissions as well as CO concentrations.

3.2.1.2 Delayed Coking

The hydrocarbon emissions from delayed coking have not been quantified. In general, hydrocarbon emissions can be minimized by venting quenching steam to a vapor recovery or blowdown system. Cooling the coke drum as much as practical will minimize hydrocarbon vaporization when the drum is opened.

3.2.1.3 Fluid Coking

The hydrocarbons in the flue gas from a fluid coking unit can be controlled by a CO boiler, which is generally used to control CO emissions from the unit.

3.2.1.4 Vacuum Distillation and Air Blowing Operations

The noncondensable hydrocarbon vapors from vacuum distillation and air blowing operations should be incinerated or vented to a blowdown system.

3.2.2 Control of Sulfur Compound Emissions

Sulfur oxides and other sulfur compounds can be emitted from sulfur recovery plants, catalytic cracking catalyst regeneration, and boiler/process heaters.

3.2.2.1 Sulfur Recovery Plants

The Claus unit is the accepted method for recovering sulfur in refineries. However, the Claus plant is not totally efficient in removing sulfur, and the tail gas from the unit can be a major source of sulfur compound emissions.

Control Options--Tail gas treating methods are available for reducing SO_x emissions to acceptable levels. No particular system is recommended; more than 70 processes have been proposed, developed, and/or commercialized.

Research and Development Needs--There is a continuing high level of research and development activity in the area of sulfur recovery and tail gas treating. This activity should be monitored periodically to identify promising emerging technologies which would be particularly applicable in petroleum refineries.

3.2.2.2 Fluid Catalytic Cracking Units

Control Options--Scrubbing of FCCU flue gases and the hydrodesulfurization of feedstocks can both reduce SO_x emissions. These methods can be very costly. The potential for use of either method as an SO_x control technique will depend on a number of complex factors including economics, regulatory requirements, secondary pollution, and sulfur levels in the feedstocks.

Research and Development Needs

(a) A comprehensive study of FCCU feed desulfurization and alternate methods of SO_x control would be beneficial in guiding regulatory efforts as well as future research and development.

(b) Amoco Oil[18] (and other companies) has reported the development of a new catalyst which reduces SO_x emissions from the regenerator. This development should be followed closely, especially if commercial tests are made.

3.2.2.3 Boilers and Process Heaters

The only currently practical method of controlling SO_x emissions from refinery heaters and boilers is to minimize the sulfur content of the fuel.

3.2.3 Control of Nitrogen Compound Emissions

Nitrogen compounds emitted from refinery sources include nitrogen oxides, hydrogen cyanide, and ammonia. Only NO_x emissions are of concern. The major source of NO_x emissions are process heaters and boilers.

3.2.3.1 Process Heaters and Boilers

Control Options--The available methods for NO_x control from refinery heaters and boilers are all combustion modification techniques. These include:

- Low excess air.
- Flue gas recirculation.
- Staged combustion.
- Burner modifications.
- Load reduction/oversize firebox.

Currently available methods for removing NO_x from flue gases are not economically practical for the numerous and relatively small process heaters and boilers found in refineries.

3.2.4 Control of Particulate Emissions

Particulate matter is emitted from FCCU regenerators, fluid coking units and process heaters and boilers. Particulate emissions from refinery heaters and boilers are relatively low.

3.2.4.1 Fluid Catalytic Cracking Units

Control Options--Three methods of controlling particulate emissions from FCCU regenerators are recommended.

(a) A combination of cyclones followed by an electrostatic precipitator is effective for controlling particulates.

(b) A scrubber in series with and downstream of cyclones is an alternative particulate control method.

(c) In some applications multistage, high efficiency cyclones can provide effective particulate control.

3.2.4.2 Fluid Coking Units

Control Options--The two recommended methods of controlling particulate emissions from fluid coking units are:

(a) Scrubbers.

(b) Electrostatic precipitators.

3.2.5 Control of Carbon Monoxide (CO) Emissions

Carbon monoxide is emitted from FCCU regenerators and from fluid coking units.

3.2.5.1 FCCU Regenerators

Control Options--Two methods are available for controlling CO emissions from FCCU regenerators.

(a) CO boilers are very effective in reducing the CO content of regenerator flue gas.

(b) High temperature regeneration combined with the use of combustion promoters is an acceptable alternative to the CO boiler for CO control.

3.2.5.2 Fluid Coking Units

Control Option--A CO boiler is recommended for the control of CO emissions from fluid coking units.

PART A

FIELD MEASUREMENT PROGRAM

A major portion of the refinery assessment program was devoted to field measurement activities. In particular, fugitive hydrocarbon emission rates from numerous source types in refineries were measured. In addition, a number of heater and process stacks were sampled. The methods used in making the field measurements are described in Section 4. The results of the sampling program are presented in Section 5.

4.0 EMISSIONS MEASUREMENTS

To fulfill the objectives of this program, as stated in Section 1.1 of this report, data on the rate and character of refinery emissions were needed. Much of these data had not been obtained. In some cases where data were available, the accuracy was unknown and/or suspect. It was, therefore, necessary for Radian to perform sampling and characterization of atmospheric emissions from petroleum refineries. Sampling programs were carried out in 13 refineries throughout the United States. The sampling methodologies used in these refineries are described in this section.

Fugitive and process emission sources were sampled. Fugitive sources were devided into two groups, baggable sources and nonbaggable sources. Baggable sources are those sources that can be completely enclosed with a "bag" to measure their emission rates. This group includes valves, flanges, pump seals, compressor seals, pressure relief valves, and drains. Baggable sources represent the majority of the sources selected for testing at each refinery.

Nonbaggable fugitive sources are those that are not amenable to sampling with bags or any other type of readily constructed enclosure. There sources are broad in area, intermittent in operation, and/or very complex in their functioning. Nonbaggable sources include drainage/wastewater systems, cooling towers, barometric condensers, coke removal operations, blind changing, sampling operations, and maintenance turnarounds. Some of these sources can only be sampled using very elaborate and complex sampling procedures and equipment. Of the nonbaggable sources, only cooling towers and units of the wastewater treating system were sampled in the current program.

Stacks or vents which were identified as possible emission points for hydrocarbons and other criteria pollutants are classified as process sources. The refinery process sources which were sampled during this program include:

- Catalytic cracking unit regenerator stacks.
- Boiler and process heater stacks.
- Sulfur recovery and tail gas treating unit stacks.
- Compressor engine exhausts.
- Fume incinerator stack.
- Fluid coker flue gas stack.

These sources were sampled for total hydrocarbons, other criteria pollutants, and characterization of hydrocarbon emissions.

4.1 Experimental Design of the Program

At the beginning of the sampling program, an experimental design was prepared to provide an optimum selection of sources to be studied. The design was modified during the course of the program. The initial design, selection procedures, and design modifications are described in detail in Appendix A (Volume 2). They are summarized in the sections which follow.

4.1.1 Refinery Selection

A number of refineries were selected for sampling. Refinery age, size, and geographical location were used as selection criteria. Differences among refineries due to their different geographical locations are seen primarily in the types of potentially hazardous materials they generate. Location influences the type and quality of the crude oil which is processed, as well as the nature and relative quantities of the manufactured products. It was not believed that the location would have a major influence on the rates of hydrocarbon emissions. Refineries were selected for sampling in the following four geographical locations:

- East Coast,
- Gulf Coast,
- Midwest/Midcontinent, and
- West Coast.

The two other principal parameters which influenced the refinery selection were size and age. Age affects the characteristics of refinery equipment, and it was thought that these characteristics might ultimately influence fugitive emission rates from this equipment.

Refinery size can have an effect on such factors as the number and type of manufactured products, the number and type of potentially hazardous species, the types of units available for sampling, the amount of effort devoted to a maintenance program, and the size of equipment. The division point between large and small references was arbitrarily set at 50,000 barrels per day. To some degree, size and refinery age are not independent of each other. There have not been many new refineries significantly smaller than 50,000 barrels per day. Therefore, refineries of interest in this program were classified as one of the following types:

- old/small,
- old/large, and
- new/large.

An old refinery was one in which the oldest operating unit was over 20 years old. New refineries had no units older than 20 years.

Emission sampling took place in 13 refineries. Eight old/large refineries, four old/small refineries, and one new/large refinery were sampled.

4.1.2 Process Unit Selection

During the formulation of the experimental design of the sampling program, operating temperatures and pressures were expected to have major effects on the frequency and rate of fugitive emissions. Many combinations of temperature and pressure can be found within refinery process units. For the purpose of selecting process units for sampling, four pressure/temperature categories were employed:

- high pressure/high temperature,
- high pressure/low temperature,
- low pressure/high temperature, and
- low pressure/low temperature.

The pressure and temperature classifications were defined as follows:

- pressure
  - high ⩾ 150 psig
  - low < 150 psig
- temperature
  - high ⩾ 100°C
  - low < 100°C

Each type of process unit (catalytic cracking, reforming, etc.) was placed in a pressure/temperature category. This classification generally reflected only the operating condition in a major equipment area, such as a reactor. In each refinery, 6 - 9 process units were selected for sampling. These units were distributed as equally as possible among the four pressure/temperature categories.

4.1.3 Baggable Source Selection

The experimental design was developed to assure the unbiased selection of representative baggable emission sources for testing. All the variables that were felt to possibly influence the emission rate from each of the baggable source types were classified into one of two groups: choice parameters and correlating parameters. A choice parameter was defined as a variable that was expected to have a significant effect on the fugitive emission rate. Thus, it was used as a category in selecting the individual sources in each refinery and process unit. The choice parameters used for each fitting type are listed in Table 4-1.

All other factors which were thought to possibly affect the fugitive emission rates (but not as strongly as the choice parameters) were used as correlating parameters. Correlating parameters were not considered in the selection process, but values of these parameters were obtained and recorded for each selected source.

After the process units were selected for testing in each refinery, the individual baggable sources were chosen in each unit. A test plan was prepared which specified the number of each source type to be tested within the range of choice parameters. For example, four control valves in gas service, 4 - 8 inches in size, might be specified in a reforming unit. Because the process units were selected to include wide ranges of temperatures and pressures, these choice parameters were not deliberately specified. It was thought that the selection of sources within a variety of

TABLE 4-1. RANGE OF CHOICE VARIABLES FOR SCREENED BAGGABLE SOURCES

Baggable Source	Choice Variable	Variable Ranges Found for Screened Sources
Valves	Pressure	-10 - 3,000 psig
	Temperature	-190 - 925°F
	Fluid State	Gas, Liquid, 2-phase
	Service	In-line, Open-ended
	Function	Block, Throttling, Control
	Size	0.5 - 36 inches
Flanges	Pressure	-14 - 3,000 psig
	Temperature	-30 - 950°F
	Fluid State	Gas, Liquid, 2-phase
	Service	Pipe, Exchanger, Vessel, Orifice
	Size	1 - 54 inches
Pump Seals	Pressure	0 - 3,000 psig
	Temperature	0 - 800°F
	Capacity	0 - 100,000 gpm
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Mechanical Seal, packed seal
	Liquid RVP	Complete range
Compressor Seals	Pressure	0 - 3,000 psig
	Temperature	40 - 300°F
	Shaft Motion	Centrifugal, reciprocating
	Seal Type	Packed, labyrinth, mechanical
	Lubrication Method	Hydrocarbon lubricant
	Capacity	0.06 - 66.0 MMSCFD
Drains	Service	Active, Wash-up
Relief Valves	Pressure	0 - 1,350 psig
	Temperature	40 - 1,100°F
	Fluid	Gas, Liquid

process units would provide a group of selected sources which operated in a wide range of temperatures and pressures. This assumption proved to be true.

With the exception of washup drains, all baggable sources were selected for testing from the piping, instrumentation, and process diagrams for each process unit. The specified number of sources in each of the various categories of choice parameters were randomly chosen and located on the diagrams. Each was given a unique identification number. This method of selecting (or preselecting) sources for testing had two important benefits. It eliminated any bias which might have resulted from visual selection in the field. It was also possible to distribute the allotted number of fittings so that a wide range of process variables could be included.

The choice parameters and selection criteria for each type of baggable source are described in more detail in the following discussion.

Valves--Approximately 250 - 300 valves were selected for testing at each refinery. All of the different hydrocarbon streams within the process unit were usually represented in the valve selection process. When there was more than one valve for each process stream (as was most always the case), valves were selected to give a variety of temperature/pressure combinations for each process stream. Valves in gas and liquid service were selected.

A distinction was made between open-end and in-line valves. The piping downstream of open-end valves is open, and leakage through the valve seat can enter the atmosphere. Examples of open-end valves are sample valves and drain valves.

However, most refinery valves are in-line. Each in-line valve was classed as a block valve or a throttling (control) valve. This valve function reflects the effects of frequency of operation and type of stem movement.

Flanges--Flanges were divided into 16 categories according to the interaction of three variables: size, fluid state (gas/liquid), and operating conditions (pressure/temperature). Approximately 100 to 750 flanges were sampled per refinery. Flange sizes ranged from two inches to more than four feet. The state of the fluid within the line was considered the characteristic state.

A separate category was established for flanges which connect end pieces to vessels and heat exchangers. Within this category of vessel/exchanger/air cooler flanges, the choice variables were pressure/temperature and fluid state.

Pumps--Approximately 100 - 125 pumps were selected at each refinery. These pumps were distributed in proportion to the total number of pumps in each inspected process unit. In addition, many spare pumps were also selected.

Choice variables for pumps were pressure/temperature, capacity, shaft motion/seal type, method of lubrication and cooling methods. Shaft direction/seal type is very significant. Pumps in three categories (mechanical, packed/centrifugal, and packed/reciprocating) were chosen to be sampled. It was thought that the volatility (or vapor pressure) of the liquid being pumped was an important parameter. Pumps handling liquids with a variety of volatilities were tested.

Compressors--Compared to most other baggable sources there are relatively few compressors in a refinery. It was thought that compressors might have relatively high leak rates. For these reasons all compressors in the selected process units were selected for testing. There were generally from 10 to 20 compressors selected in each refinery.

The method of lubrication of packed seals and the type of shaft seal were important considerations in the categorization of compressor seals. Packed seals without external liquid lubrication allow leakage of light hydrocarbons; lubricated seals primarily leak heavy hydrocarbons. Mechanical seals usually require a lubricating/sealing fluid.

Pressure Relief Devices--Only those pressure devices which vented to the atmosphere were selected for sampling.

There are two types of pressure relief devices. Those in liquid service generally open in proportion to the pressure applied to them; those in gas service generally pop open when a set pressure is exceeded. Very few pressure relief devices in liquid service vent to the atmosphere. Only pressure relief valves in gas service were selected for testing.

Process Unit Drains--Two types of drains were inspected during the program. These included active drains (those used to drain various process streams) and washup drains. Although the location of active drains was not usually indicated on the process flow diagrams, these drains were still selected before entering the unit by selecting drains associated with pumps, towers, vessels, and other processing equipment. The location of washup drains, however, could not be predicted and these drains were selected after entering the process unit.

After the preselection process was completed, each of the selected sources was physically located in the refinery process units. They were tagged with the appropriate identification number. When preselected sources were found to be nonexistent or physically inaccessible, alternate fittings were selected from the piping, instrumentation, and process flow diagrams.

4.1.4 Selection of Nonbaggable Sources

Cooling towers, oil-water separators, and dissolved-air flotation (DAF) units were the only nonbaggable source types which were sampled during this program. The experimental design of the program called for the sampling of any of these devices which were associated with the selected process units in each refinery. Sources were not selected if any of the following occurred:

- Adequate sampling points were not available or accessible.
- The unit was not representative of normal refinery practice.
- Data required for the calculation of emission rates was not available.

The nonmethane hydrocarbon emission rate from these nonbaggable sources was calculated by material balance around each unit.

4.1.5 Selection of Process Sources

Process sources (stacks and vents) were selected for sampling in the majority of refineries. Three stacks were to be chosen in each refinery. One of these was to be a fluid catalytic cracking unit stack. The other two were to be stacks from heaters/boilers, sulfur recovery or tail gas treating units, compressor engine exhausts, air blowing units, fluid coking units, or incinerators. In each refinery, the individual stacks were selected on the basis of availability (sampling ports, platforms, accessibility, etc.) and the need for data from a variety of process source types.

4.1.6 Modification of the Original Experimental Design

The emissions data were analyzed continuously during the sampling program. The results of these analyses were used to modify the experimental design of the program to obtain the most useful data within the budgetary and time constraints of the program. The selection procedures for the various source types were modified as described below.

Baggable Sources--As the program progressed, it was found that those fugitive emission sources in gas or volatile liquid services tended to leak with a greater frequency and a higher leak rate than those sources handling less volatile materials. The selection process was modified to include a higher proportion of valves and pump seals in gas and volatile liquid service.

It was also found that only a small fraction of flanges leaked and the emission rates were low. The number of flanges selected for testing was drastically reduced in the latter stages of the field program.

In the last four refineries that were visited, a study was performed to evaluate the effects of simple maintenance on the reduction of emissions from leaking valves. Three variables were considered in selecting valves for the study. These were:

- Leak rate - leak rates (as estimated from screening values) were classified into one of three ranges. Valves in each leak rate range were selected for testing in each refinery (if they were available).

- Process stream type - process streams were divided into three categories, according to their volatilities (gas streams, hydrocarbon liquids with vapor pressures above 0.1 psia at 100°F, and hydrocarbon liquids with vapor pressures below 0.1 psia at 100°F). Valves in each type of stream service were chosen for the study.

- Valve type - valves in four categories were studied. The four categories were (1) block valves (gate valves), (2) block valves (valve types other than gate valves), (3) control valves (globe valves), and (4) control valves (valve types other than globe).

A selective experimental design based on categories of the above variables was used to minimize the number of valves required in the study. Maintenance was performed on a total of 86 valves.

Nonbaggable Sources--In the latter stages of the field sampling program, no more nonbaggable sources were selected for sampling. Cooling tower emissions were found to be low and sampling of cooling towers was discontinued. The methods used to determine hydrocarbon emission rates from oil-water separators were found to be unsatisfactory. Sampling of these sources was discontinued in the last four tested refineries.

Process Sources--In some refineries, three stacks (as suggested in the experimental design) with adequate sampling facilities could not be located. In these cases, only the available stacks were sampled. Additionally, because of cost and time constraints, no stacks were sampled in the final four tested refineries.

4.2 Sampling Methodology

In this section, the methodologies used in sampling emissions from baggable, nonbaggable, and process sources is described. In the case of baggable sources, a screening procedure was used prior to selecting sources to be sampled.

4.2.1 Baggable Source Screening Procedure

To minimize the number of baggable sources which had to be sampled, a preliminary hydrocarbon monitoring or "screening" was carried out at each selected source. Those sources which were found to have hydrocarbon concentrations (screening values) above 200 ppmv were selected for possible emissions sampling. Any selected source which had a screening value below 200 ppmv was considered to be a "nonleaking" source. As the data base was expanded, the screening value limit of 200 ppmv was found to correspond to a leak rate in the order of 0.0001 pounds per hour.

All the choice and correlating variables were recorded for all sources that were screened.

A Bacharach Instrument Company J-W Model TLV Sniffer was used to screen baggable sources. This instrument uses a catalytic combustion detector to measure hydrocarbon concentrations as low as 1.0 ppm. Readings could be obtained as high as 100,000 ppm read as ppm hexane by volume. A second instrument, the Century Instrument Company Organic Vapor Analyzer Model OVA-108, was also used to screen for hydrocarbon vapors. However, for consistency, sources identified with this instrument were rescreened with the TLV Sniffer when the source was sampled. The Century instrument utilizes a flame ionization detector.

The procedure used for screening with the TLV Sniffer was quite simple. The sample probe was held as close as possible to the suspected leak source. This reduced the effect of the wind and increased the reproducibility of the readings. The screening procedure differed slightly for each baggable source type as discussed below.

4.2.1.1 Valves Screening Method

Most of the valves that were selected for screening were either gate, globe, or control valves. Hydrocarbon leaks from these valves occur at the stem and/or the packing gland. Some plug valves were also selected. Hydrocarbon leaks from this type of valve can occur at the plug square or under the malleable gland.

Both the stem and the packing gland of selected valves were screened. The probe locations used included the four arbitrary compass points around the seal, relative to the valve casing. Thus, a total of eight such readings were taken for each valve. In addition, two more readings (one for the stem and one for the glands) were obtained at a distance of 5 cm (using a wire extension as a guide) from the leak source. When screening at 5 cm, the probe was rotated in a circular path around the leak source. Only the maximum reading was recorded in these cases.

4.2.1.2 Flanges Screening Method

Flanges were screened by placing the TLV Sniffer probe at two-inch intervals around the perimeter of the flange. After locating the maximum leak point, three additional readings were taken at the remaining compass points, relative to the location of the maximum leak point. All four readings were recorded.

4.2.1.3 Pump and Compressor Seal Screening Method

Pump seals were screened in a manner similar to that used for screening valves. Leakage occurs around the rotating shaft at the point where it enters the pump housing. The Bacharach TLV Sniffer probe was placed as close as possible to the potential leak point around the shaft at the pump housing. Four readings were taken at points 90 degrees apart around the shaft. Hydrocarbon concentrations of 200 ppm or greater at any of the four points resulted in the pump being bagged and sampled.

Large pumps or pumps in severe services may have two seals, an inboard seal and an outboard seal. In these cases, each seal was screened separately.

The screening procedure for compressors depended on the accessibility of the seal area. If the seal area was accessible, the screening procedure was identical to that for pumps. The TLV Sniffer probe was placed at four locations 90 degrees apart around the shaft and right at the point where the shaft enters the compressor housing. A hydrocarbon concentration of 200 ppm or more at any point indicated the need for bagging and sampling of the seal.

In many cases the seal area was enclosed and hydrocarbons leaking from the seal were vented to the atmosphere or to a vapor recovery system. When compressors vented to the atmosphere were encountered, they were screened, if possible, at the point where the vent pipe discharged to the air. The TLV probe was positioned at a point located just inside the end of the vent. A hydrocarbon concentration of 200 ppmv or greater indicated the need for sampling.

Compressors often have more than one seal. Each seal was individually screened.

4.2.1.4 Pressure-Relief Valve Screening Method

Only those pressure-relief devices that are vented to the atmosphere were screened. Those devices that are vented to blowdown and flare systems can only leak to the atmosphere at the connecting flanges, and these leak sources are considered to be flanges.

The relief valves were screened using the Bacharach TLV Sniffer. The probe was placed at two-inch intervals around the perimeter of the vent (horn) just at the exit. The probe was also placed at the center of the vent opening at a level with the vent exit. When the top of the horn was inaccessible, a screening value was obtained at the weep hole, located near the bottom of the horn. The maximum TLV readings were recorded. If any readings exceeded 200 ppm, the relief device was to be sampled and bagged.

4.2.1.5 Drain Screening Method

In this program, process unit drains were classified as either active or washup drains. The screening process is the same for both types.

The probe of the Bacharach TLV Sniffer was placed at two-inch intervals around the perimeter of the drain. At each of these points, the probe was placed right at the inside edge of the drain at the level of the exit. The maximum concentration was recorded.

Upon completing the traverse around the perimeter of the drain, one additional reading was taken at the center of the drain. The maximum of the perimeter and center readings was recorded and used as the basis for sampling decisions. If the maximum individual value was equal to 200 ppmv hydrocarbon or greater the drain was bagged and sampled.

4.2.2 Sampling Emissions from Baggable Sources

The method preferred for sampling emissions from baggable sources is the dilution or flow-through method. The sampling trains that were used in this method are shown in Figure 4-1. The train was contained on a portable cart, which could be easily pushed around the process units from source to source.

The major equipment items in the sampling train were the vacuum pump used to draw air through the system, and the dry gas meter used to measure the flow rate of gas through the train. The main vacuum pump was a 4.8 CFM Teflon-ring piston-type pump equipped with a 3/4 horsepower air-driven motor. It can maintain a maximum flow rate of 2.5 CFM. The dry gas meter was a Rockwell Model 1755 Test Gas Meter with a Number 83 Test Index.

Other equipment items in the train include Whitey valves, copper and stainless steel tubing, Teflon hose, thermometers, mercury and water manometer, a cold trap, and a small air-driven diaphragm sampling pump.

The cold trap was placed in the system to condense water and hydrocarbons. Downstream condensation in the lines and sampling train was thus avoided. The cold trap was simply a 500 ml flask in an ice bath, placed very close to the enclosure. The collected condensate consisted of water and, in some cases, organic material.

The leak source is shown as a valve in Figure 4-1. However, the same sampling train was used for all baggable source sampling with the flow-through technique. The size and shape of the leak source enclosure (bag) was changed and adjusted to fit each particular source shape and operating condition.

Each leak source enclosure (bag) was made of 1.5 to 5 mil Mylar®. Mylar® does not significantly adsorb hydrocarbons, is very tough, and has a high melting point. Each enclosure was kept as small as possible and was connected by means of a bulkhead fitting and Teflon hose to the sample train. A separate line was connected from the tent to a magnahelic to

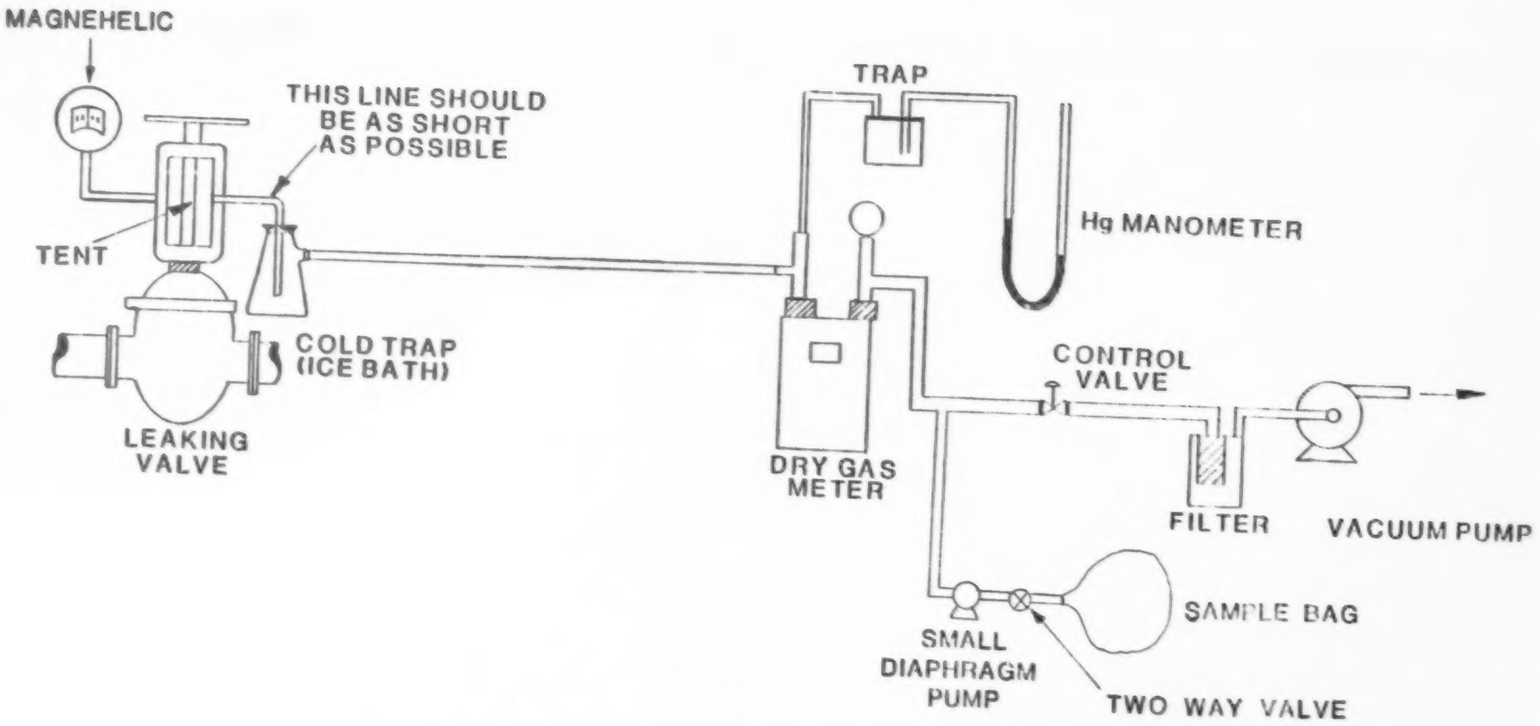

MAGNEHELIC
THIS LINE SHOULD BE AS SHORT AS POSSIBLE
TENT
COLD TRAP (ICE BATH)
LEAKING VALVE
TRAP
Hg MANOMETER
DRY GAS METER
CONTROL VALVE
FILTER
VACUUM PUMP
SAMPLE BAG
SMALL DIAPHRAGM PUMP
TWO WAY VALVE

Figure 4-1. Sampling Train for Baggable Sources of Hydrocarbon Emissions

allow for continuous monitoring of the pressure inside the tent. A slight vacuum was maintained inside the tent while air was being pulled through to insure that hydrocarbons did not escape.

Important considerations in constructing each source enclosure were the metal skin temperature in the enclosed area and in the area of the seal, the presence or absence of supports for the tent, and possible interference with working parts. At skin temperatures of 400°F or less, seals could be made with duct tape; at higher temperatures, metal foil and asbestos insulating tape were used. Further details of enclosure construction for specific sources are given in Appendix A (Volume 2).

During each sampling effort, the vacuum pump was started, and the entire system was allowed to come to equilibrium. The Bacharach TLV Sniffer was used to monitor the effluent air from the sampling train to assure that equilibrium had been established.

The air flow rate, temperature, and pressure at the dry gas meter were recorded during each sampling run. When equilibrium was established, samples of the gas passing through the sampling train were taken.

In most instances an evacuated Mylar® sample bag which had previously been completely flushed with air was attached to a two-way valve in the sampling line. The bag was first flushed with sample gas. Then the sample bag was filled with 5 - 7 liters of gas. While this sample bag was being filled, another bag was being filled by a large plastic syringe with ambient air from near the tent. The bags and the cold trap, removed from the train and sealed, were sent to the mobile laboratory for analysis.

The air sample was analyzed for the total methane and nonmethane concentration. The quantity of any organic condensate collected in the cold trap was measured. The total nonmethane hydrocarbon emission rates were calculated from the air flow rate, nonmethane hydrocarbon concentration, and the volume or weight of organic condensate.

The above method was altered for special cases. For large leaks, the vacuum pump was disconnected from the sampling train and the sample gas allowed to pass through the sample train (including the cold trap) and exit immediately downstream of the dry gas meter. The flow rate through the dry gas meter can be combined with the amount of organic condensate (if any) to obtain a direct measure of the hydrocarbon vapor leak rate.

Liquid leaks, in which no vapor leakage could be detected, were treated as vapor leaks if the liquid vaporized immediately. If the liquid ultimately vaporized, it was collected in a cooled, covered graduated container. When water or water vapor was present in a gas sample, it was condensed in the cold trap and did not interfere with hydrocarbon analysis.

4.2.3 Sampling of Nonbaggable Emission Sources

Nonbaggable sources which were sampled during this program include oil-water separators, dissolved air flotation (DAF) units, and cooling towers. Fugitive emissions from these sources were estimated from a volatile hydrocarbon mass balance around the unit. The difference between the volatile hydrocarbon content of the liquid influent and the volatile hydrocarbon content of the liquid effluent was assumed to equal the fugitive hydrocarbons emitted to the atmosphere.

4.2.3.1 Oil-Water Separators

The API separator is the most widely used type of oil-water separator; sampling methods developed for it could be used for other types as well. In large refineries with more than one separator, each separator was sampled individually.

Inlet liquid to the separator was obtained from the separator inlet line or from the separator itself at a point as near to the inlet as possible. The inlet liquid was a heterogeneous mixture of oil and water. A representative sample was difficult if not impossible to obtain.

Three streams normally exit from a separator: the oil skimmed from the surface of the water, the water itself, and a sludge stream. The sludge was not considered a significant source of atmospheric emissions for several reasons.

- It is normally not exposed to the air in the separator.
- Any volatile material in the sludge would have to pass into the water and then into the oil layer on top of the water before it could be emitted to the atmosphere.
- The water, being well mixed with the oil and sludge at the separator, was assumed to be saturated with volatile hydrocarbons at all points in the separator.
- The loss of volatile material from the oil phase on the surface of the separator liquid was thought to be very much greater than that from the water itself. In many cases, the water was completely covered by a layer of oil up to several inches thick.
- The volatile hydrocarbon content of the inlet and outlet oil streams was determined after sludge had been centrifuged from the samples. Only the

centrifuged oil samples were analyzed for volatile hydrocarbons.

The sludge phase was not sampled.

Skimmed oil samples were taken at the outlet of the pump to the slop-oil tank, in the skim pipe, in the line from the separator to the slop-oil tank, and from the slop-oil tank itself. Water samples were taken at several points along the overflow weir and composited. Samples were taken in tightly-capped glass bottles from each stream several times a day for several days. Samples from each source were composited daily.

4.2.3.2 DAF Units

Dissolved-air flotation (DAF) units process water from the oil-water separators. Some are partially enclosed and others are completely open. Only the water phase from the oil-water separator carries a significant amount of hydrocarbons into the DAF unit. The separator outlet samples were used as the DAF inlet water sample. The outlet water stream was sampled at the overflow weir. Water samples were taken several times a day for several days and composited daily for each source. The froth layer was not sampled. This layer was exposed to the air for only a short time. No rates for froth removal could be determined.

4.2.3.3 Cooling Towers

Water enters a cooling tower from two sources: make-up water and the hot water from process exchange. Water leaves the tower as vapor from the top of the tower, as cooled water returning to process exchange, and as blowdown. There is also some loss from windage and drift. Make-up water exactly equals blowdown plus evaporation, therefore only the incoming hot water and the exiting cool water had to be sampled. The blowdown stream was considered to have the same volatile hydrocarbon content as the cool water leaving the unit (or in the basin). The blowdown stream was considered in the overall hydrocarbon material balance.

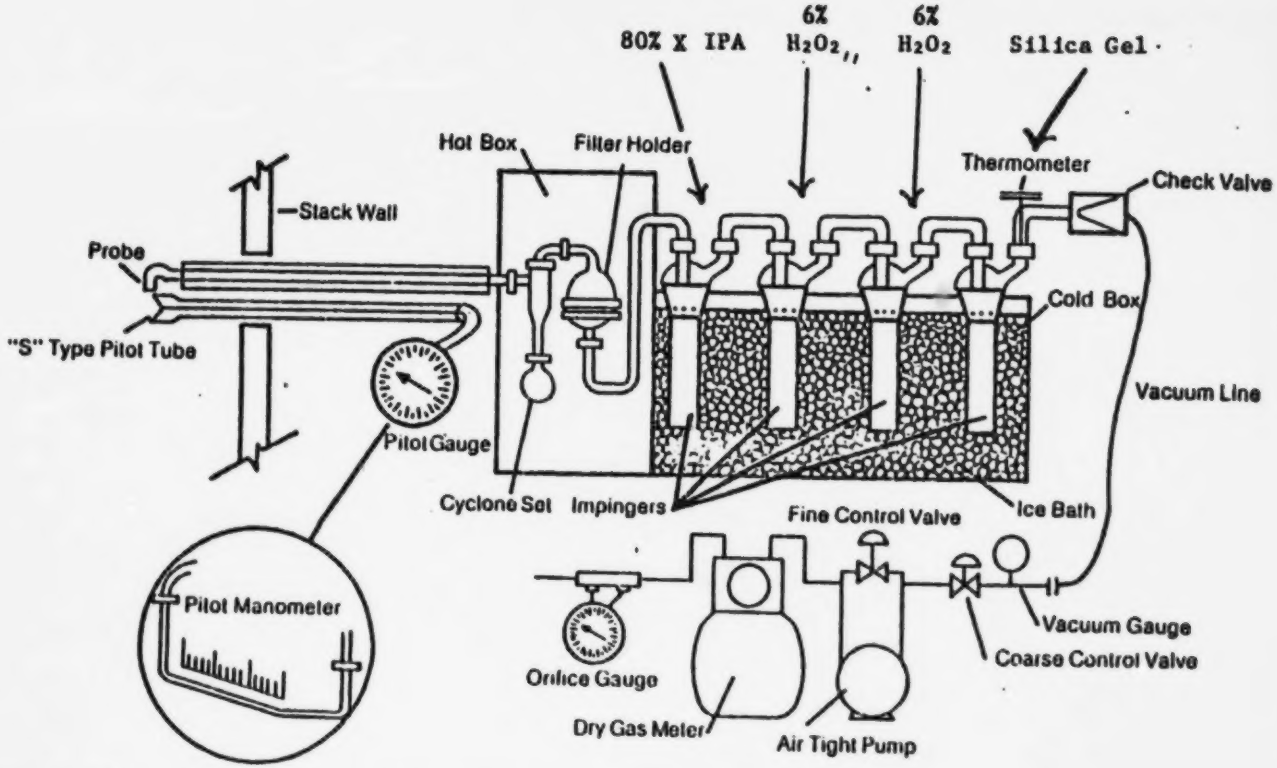
Inlet water was sampled from one of the many small sampling valves which normally branch off the large cooling water return risers. Outlet water was taken from the water flowing downward through the tower at a location just above the level of the cooling tower basin. All samples were kept in sealed bottles under refrigeration until analysis.

4.2.4 Sampling of Process Sources (Stacks and Vents)

In general, stacks and vents were sampled for a determination of total hydrocarbons, a speciation analysis, and analyses for other criteria pollutants on an as-needed basis. Samples were taken from catalytic cracking unit regenerator stacks, sulfur recovery or tail-gas treating unit stacks, process heater stacks, fluid coker stacks, and an incinerator stack. Measurements made on these samples included some or all of the following: EPA Reference Methods 1, 2, 3, and 4 on all stacks;[20] methane and nonmethane hydrocarbons on all stacks; particulate and vapor collection for organic characterization on one stack; and sulfur gases on the sulfur recovery and/or tail-gas treating unit stack.

Stack sampling procedures were a combination of EPA approved methods for criteria pollutants[20] (SO_2, SO_3, and particulates); EPA Level 1 screening procedures[21] (SO_2, COS, CS_2, H_2S, NO, NO_x, "organic vapor"); Texas Air Control Board methodology;[22] and, Radian-devised methods (HCN, NH_3, THC). Figures 4-2 through 4-4 depict the sampling trains used. Methods for individual species are given below.

Particulates--Particulate samples were collected from each stack according to EPA Reference Method 5.[20] A Lear-Sigeler, Inc., stack sampling train was used. Sampling was performed isokinetically along two


80% X IPA
6% H_2O_2
6% H_2O_2
Silica Gel
Hot Box
Filter Holder
Thermometer
Check Valve
Stack Wall
Probe
"S" Type Pilot Tube
Cold Box
Vacuum Line
Pilot Gauge
Cyclone Set
Impingers
Fine Control Valve
Ice Bath
Pilot Manometer
Vacuum Gauge
Coarse Control Valve
Orifice Gauge
Dry Gas Meter
Air Tight Pump

Source: Lear Siegler, Inc., PM 100 - Operation & Maintenance Manual.

Figure 4-2. Method 5 Train for SO_2 and Particulates

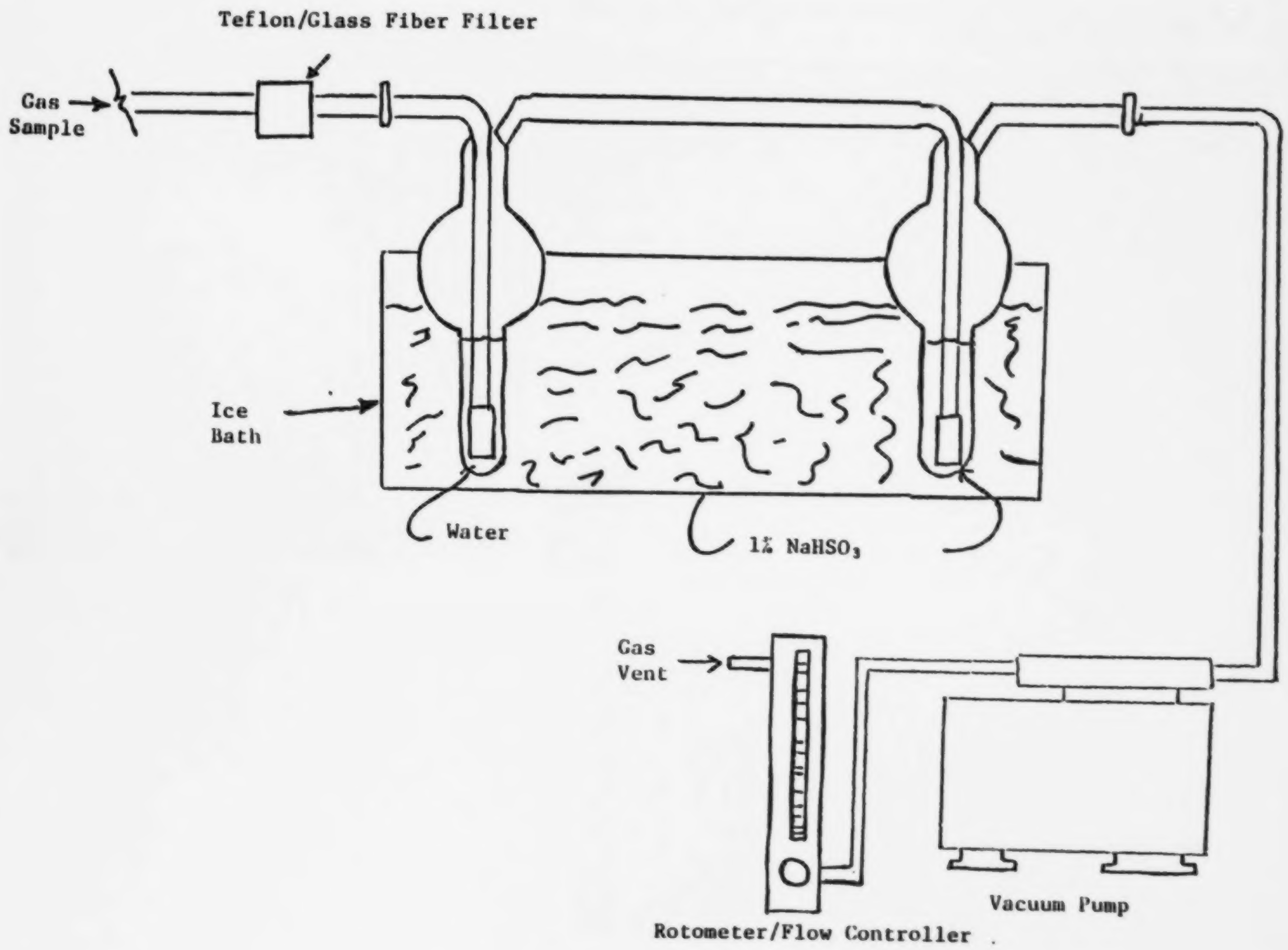

Teflon/Glass Fiber Filter
Gas Sample
Ice Bath
Water
1% NaHSO$_3$
Gas Vent
Rotometer/Flow Controller
Vacuum Pump

Figure 4-3. Aldehyde Impinger Train

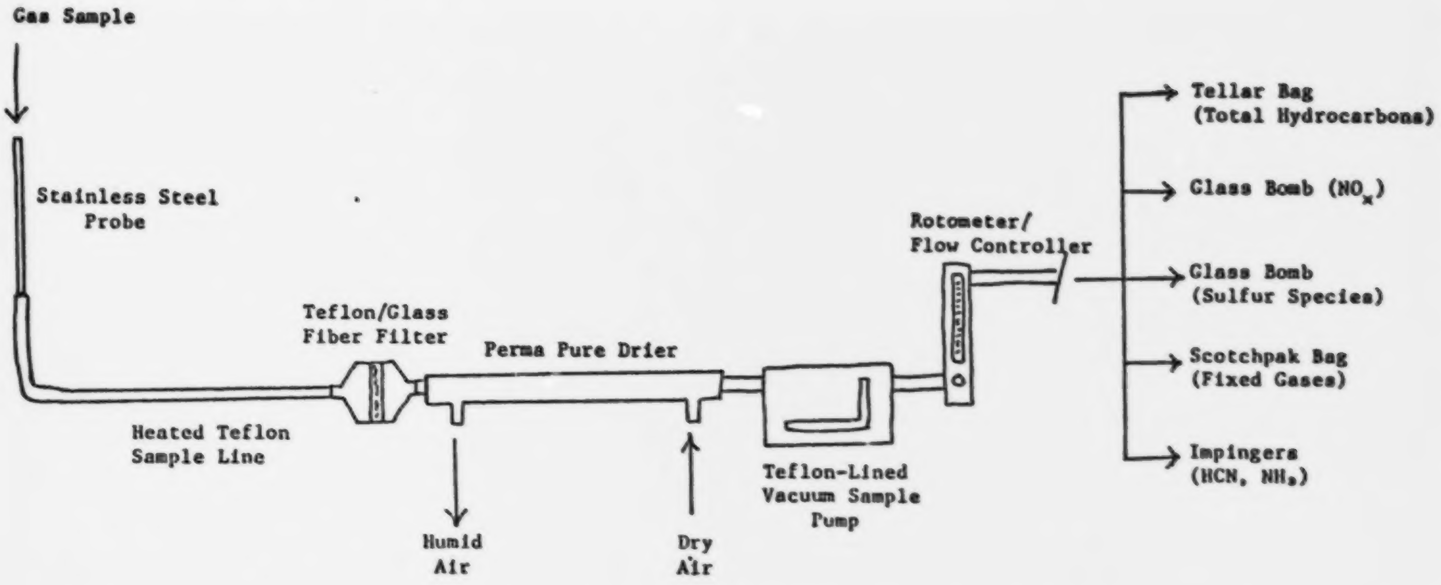

Gas Sample
Stainless Steel Probe
Heated Teflon Sample Line
Teflon/Glass Fiber Filter
Perma Pure Drier
Humid Air
Dry Air
Teflon-Lined Vacuum Sample Pump
Rotometer/ Flow Controller
Tellar Bag (Total Hydrocarbons)
Glass Bomb (NO_x)
Glass Bomb (Sulfur Species)
Scotchpak Bag (Fixed Gases)
Impingers (HCN, NH_3)

Figure 4-4. Grab Sample Collection and Preparation System

perpendicular traverses of each stack. Duplicate sample runs were made on each stack if possible.

$\underline{SO_x}$--Oxides of sulfur (SO_3 and SO_2) were collected according to EPA Reference Method 8.[20] Collection was done during each particulate collection run by passing the filtered sample gases through an impinger train consisting of an 80 percent isopropanol impinger for SO_3 collection followed by two six percent aqueous hydrogen peroxide impingers for SO_2 collection and a silica gel impinger. The total mass of water collected in this train was used to determine the moisture content of the stack gas.

Aldehydes--The aldehyde train (Figure 4-3) consisted of two ice-cooled impingers, each containing 10 ml of a 1.0 percent aqueous sodium bisulfite solution. Approximately 12 liters of stack gas were drawn through each impinger train at a rate of 200 ml per minute. A stainless steel probe was inserted into the stack to a point of average velocity, then the gas was transferred to the impinger train by a small vacuum sampling pump through a heated Teflon sample line equipped with a Teflon particulate filter.

A second impinger sampling train was sometimes used to sample for total aldehydes. It consisted of three ice-cooled impingers, the first containing 10 ml water and the following two containing 10 ml of 0.05 percent aqueous 3-methyl-benzothiazolone hydrazone (MBTH) solution. The aldehydes were collected by dissolution in the water and reaction with MBTH to form a water-soluble adduct. Approximately 12 liters of stack gas were drawn through the impinger train at a rate of 200 ml per minute.

NCH and NH_3--Hydrogen cyanide was collected with the Method 5[20] stack sampling equipment by passing the filtered sample gases through three impingers containing 2.0 N sodium hydroxide. Ammonia was collected similarly by using three impingers containing 0.1 N sulfuric acid. In each case, sampling was conducted over thirty-minute periods and resulted in approximately 10 SCF of gas for each sample.

Grab Samples--The remaining four categories of species were all collected by grab sampling techniques. A stainless steel probe was inserted into the stack to the point of average velocity, and the sample gas drawn out through a heated Teflon sampling line. The sample passed through a heated Teflon glass/fiber filter to remove particulates, then through a permeation drying system to remove moisture. The Perma-Pure Products, Inc., multi-tube drier has been found to effectively remove moisture down to 100 ppm while causing only a 1 - 3 percent loss of the desired species. Movement of the sample through the system was accomplished by a miniature Thomas vacuum pump equipped with Teflon heads and diaphragm. The outlet stream from the pump was directed to the several bags and bombs used to transport the samples to the field laboratory for analysis.

Samples for methane and nonmethane hydrocarbons analysis were collected in 4-liter Tedlar sample bags.

Samples for fixed gases (CO_2, N_2, H_2, O_2, CO) analysis were collected in aluminized Scotchpak sample bags. These species are quite unreactive and are not prone to adsorb onto the bag walls significantly.

The sulfur species (CS_2, H_2S, COS, and SO_2) proved to be the most difficult to collect and transport. Samples for analysis of these species were collected in glass bombs.

Samples for NO_x analysis were collected in evacuated 2 liter glass flasks to which had been added 25 ml of a potassium dichromate-aqueous sulfuric acid solution.

4.2.5 Sampling for Organic Species Identification

A minimum number of samples were taken for species identification and quantification. The number of samples taken from a particular stream depended on the likelihood of the presence of potentially hazardous materials. The relationship between the composition of a vapor leak and the composition of the stream from which it came was investigated by taking both liquid and vapor speciation samples wherever possible. A listing of the streams sampled for speciation studies is included in Appendix A (Volume 2). The sampling methodology discussed briefly below is explained in more detail in Appendix A (Volume 2).

Vapor Samples--Vapor samples were collected by passing the leaking vapor through an adsorbent tube. Tenax was used to adsorb volatile organics in the acetone-to-naphthalene range. Charcoal was occasionally used for the 250°F to 300°F boiling range materials. High molecular weight fugitives, heterocyclic nitrogen + sulfur compounds, and polynuclear aromatics were trapped with XAD-2 resin. Operating parameters for the use of these sorbents are given in Table 4-2.

In the "blow-through" method, plant air (compressed air) was charcoal filtered and blown into the enclosure around the leaking source. An outlet line was provided on the enclosure, and air exited through this line.

A separate sample line was connected to the enclosure outlet line. Air was drawn through the sample line with a vacuum pump. The air first passed through a glass knockout flask to remove any entrained condensate. The air was then drawn through tubes packed with either XAD-2 resin, charcoal, or Tenax adsorbent and finally the air was drawn through a dry gas meter.

TABLE 4-2. NOMINAL OPERATING CONDITIONS FOR SAMPLING WITH ADSORBENTS

Sorbent	Detection Limit	Method	Recommended Ranges			
			Volume	Flow	Mass	Inlet Concentration
Tenax	~1 ppb	GC-MS	1-2 ℓ	10-25 ml/min	50-100 ng minimum	5-20 ppbv(minimum)
Charcoal	~500 ppb	GC-MS	5-10 ℓ	20-50 ml/min	2-15 mg	200-500 ppmv
	~50 ppm	GC				
XAD-2	~50-100 ppb	GC-MS	300-600 ℓ	5-10 l/min	3-4 G maximum	100-1000 ppmv

The "draw-through" method (as in Figure 4-1) for taking vapor samples on adsorbents differs from the "blow through" method in only one way. Instead of blowing air through the enclosure around the leaking source, ambient air is drawn into and through the enclosure with a vacuum pump.

All adsorbent tubes were sealed and frozen until they could be analyzed.

Liquid Samples--Samples of various representative liquid streams were collected from sampling points along the processing lines. All samples were taken in Pyrex sample bottles, tightly sealed with Teflon-lined screw caps, and refrigerated until analysis.

Stack Samples--Stack samples were collected for organic speciation with the use of a modified Aerotherm Source Assessment Sampling System (SASS). A canister of XAD-2 resin replaced the original-equipment organic concentrator.

A 1,000 - 1,200 SCF sample of stack gas was drawn from a point of average velocity in the stack. Particulates were removed on a filter, the gas was cooled, then nonvolatile organic compounds were removed by the XAD-2 resin. The particulates, the condensate from cooling the gas, and the resin were collected for analysis.

4.3 Analytical Methodologies (Field Laboratory)

Analyses were done on-site in a mobile laboratory for methane and nonmethane hydrocarbons, NO/NO_x, sulfur gases, aldehydes, ammonia, and cyanide. These are described in detail in Appendix A (Volume 2).

4.3.1 Hydrocarbon Measurement

The methane and nonmethane hydrocarbon content, and therefore total hydrocarbon content, of baggable emission gas samples was determined with the use of a Total Hydrocarbon Analyzer (THC) Model 301C made for Radian by Byron Instruments.

The THC analyzer had a flame ionization detector for measurement of hydrocarbon concentration. It produced a linear readout in the 0 - 2 to 0 - 20,000 ppmw ranges. Dilution techniques were used for more concentrated samples. Hydrocarbon-free air was used as the carrier gas. Baggable samples were analyzed by pumping sample directly from the sample bag to the sample loop of the instrument with the use of an integral pump in the instrument. A detailed description of the theory and operation of this instrument is contained in Appendix A (Volume 2).

Oil layer samples and wastewater samples were analyzed on-site for volatile organics, since only volatile components are lost to the atmosphere as fugitive emissions.

To determine the volatile content of the oil samples, a small amount of the material was placed in an open container and stired for eight hours. The volatile content was represented by the change in sample weight over the test period.

Purgeable organics were swept from the water samples into Teflon sampling bags. The contents of the bag were analyzed on the THC analyzer described above.

The total organic carbon content of water samples was determined with a Dohrmann DC52D TOC Analyzer. This instrument oxidized organics to carbon dioxide, then reduced the carbon dioxide to methane. The methane was measured with a flame ionization detector.

4.3.2 NO/NO_x Determination

Nitrogen oxides (NO and/or NO_2, or collectively, NO_x) in stack gases were determined as nitrate (NO_3^-) colorimeterically. The sample was collected in a glass flow-through bomb. The NO_x in the sample was converted to nitrate ion by reaction with hydrogen peroxide injected immediately following collection of the sample. A yellow color was developed in the mobile laboratory by the addition of potassium hydroxide and phenoldisulfonic acid as part of a set procedure. The intensity of the color, as measured by a Bausch and Lomb Spectronic 21 spectrophotometer, was compared against a set of standards to determine NO_x content.

The procedure is accurate to within ± 3 percent for nitrate concentrations in the 10 - 20 ppm range; ± 2 percent for the 20 - 60 ppm range. Samples with more than 60 ppm nitrate were diluted. This method is described further in Appendix A (Volume 2).

4.3.3 Sulfur Gases

Separate analyses for SO_2 and SO_3 were performed on the impinger samples collected during each EPA Method 5 train operation. An 80 percent isopropanol impinger collected samples for SO_3 analysis; two 6 percent H_2O_2 impingers were used for SO_2 analysis. SO_2 and SO_3 were converted to H_2SO_4 in the impingers. The contents of these impingers were titrated with barium perchlorate to a Thorin indicator end-point (yellow color) as specified in the EPA Reference Method 8.[20] The amount of sulfate found indicated the amount of SO_2 or SO_3 in the original sample.

4.3.4 Aldehydes

The contents of the one percent bisulfite impinger shown in Figure 4-3 were analyzed for aldehydes. The aldehydes collected in these impingers formed an aldehyde-bisulfite complex with the bisulfite. When the sample was to be analyzed, excess bisulfite was destroyed with an excess of iodine. The excess iodine was destroyed by the addition of thiosulfate, which was then titrated to a faint blue end-point. Addition of a carbonate buffer solution released the complexed bisulfite. The released bisulfite was titrated with iodine to a final end-point. The amount of iodine titrant in the final titration indicated the amount of aldehydes as formaldehyde in the solution.

4.3.5 Ammonia

Ammonia was collected from gas streams in impingers containing sulfuric acid at a pH < 2. These impingers were part of the sample train pictured in Figure 4-4. The contents of the impingers were then buffered with sodium hydroxide and sodium tetraborate to a pH of 9.5. Ammonia was then driven from the samples and bubbled through a boric acid indicating solution which changed color on reaction with ammonia. The boric acid was then titrated to its original color with a standard sulfuric acid solution. The amount of sulfuric acid titrant required indicated the amount of ammonia present in the original solution.

This method for NH_3 analysis has no known interferences and is considered very accurate to 0.05 ppm.

4.3.6 Cyanide

Cyanide was collected in impingers containing sodium hydroxide at a pH > 12. These impingers were part of the sample train shown in Figure 4-4. The contents of the impingers were first tested for the presence of oxidizing agents and sulfide. Any oxidizing agents were removed with ascorbic acid; sulfides were precipitated with lead nitrate and filtered off. A distillation procedure was then used to separate CN^- from other cyano compounds. The CN^- concentration in the resultant solution was determined colorimetrically on a Bausch and Lomb Spectronic 21

Spectrophotometer with the use of pyridine-barbituric acid, which forms an intense blue color with free cyanide.

4.4 Identification of Emitted Species

Analyses for organic species were performed in Radian's Austin laboratory. Inorganic analyses were performed by Commercial Testing and Engineering.

4.4.1 Qualitative Organic Analyses

Trace organic species concentrations were determined by gas chromatography/mass spectroscopy (GC/MS) techniques for the samples listed in Table 4-3.

TABLE 4-3. SUMMARY OF ORGANIC SAMPLES FOR QUANTITATIVE ANALYSES

Sample Type	Sample Composition	Emission Source
Process Liquid	Organic Liquid	Fugitive
XAD-8 Resin	Sorbed Organic Vapor	Fugitive
Tenax	Sorbed Organic Vapor	Fugitive
XAD-2 Resin	Sorbed Organic Vapor	Point
Particulate	Particulate	Point
Effluent Water	Aqueous	Point
Charcoal	Sorbed Organic Vapor	Fugitive

Preliminary treatment of GC/MS samples included isolation of the species of interest, separation of the isolated species into groups with similar chemical or physical properties, and concentration of the species of interest. Each sample required some or all of these preliminary treatments.

Isolation--Organic species were isolated by solvent extraction or thermal desorption. Organics from particulate and XAD-2 resin samples were isolated by Soxhlet extraction with diethyl ether; XAD-8 resin samples were separated by Soxhlet extraction with pentane. Pentane was also used as the solvent for process liquids. Aqueous samples were manually extracted with diethyl ether in a separatory funnel.

At the conclusion of the isolation phase, the process liquid and XAD-8 resin samples were ready for analysis. The effluent water samples remained to be concentrated. The XAD-2 resin and particulate samples were further separated as described in the following section.

The organics in the Tenax tubes were thermally desorbed directly into the GC/MS system by a Tekmar Liquid Sample Concentrator. This process is an integral part of the analysis itself.

Separation--Radian developed an acid-base-neutral (ABN) separation strategy for the separation of complex environmental samples. This strategy was used for the particulate and XAD-2 resin samples. It was based on a series of liquid-liquid extractions that separate a sample into three principal fractions:

A: organic acids whose salts partition into water at a high pH,

B: organic bases whose salts partition into water at a low pH, and

N: neutral hydrophobic compounds.

These principal fractions were then further subdivided into a total of seven fractions to be analyzed by GC/MS.

This separation scheme was not intended for the isolation of every compound collected in a particular sample; its purpose was to effect a sufficient division of organic components so that those compounds of primary interest could be identified and quantified.

The complete separation scheme is presented in Appendix A (Volume 2). In brief, the acidic and neutral components of the sample were extracted from the basic component with acidic water. Basic components were extracted from the aqueous phase with ether, concentrated, then transferred to a hexane medium and reconcentrated. The hexane concentrate was transferred to a silica gel column and divided into four fractions: nonpolar neutrals, moderately polar neutrals, polar neutrals, and very polar neutrals.

The acid/neutral component was basified. The extract containing the neutral species was dried and concentrated. The alkaline extract containing the acidic compounds was methylated in two steps to convert phenols to methyl ethers and carboxylic acids to methyl esters. Dimethyl sulfate was used for the phenols and diazomethane for the carboxylic acids.

Concentration--Each extract was concentrated with macro and micro Kuderna-Danish (K-D) concentrators before analysis. Typically, a sample was concentrated to 5 - 10 ml in a macro K-D, then to 1 ml in a micro K-D.

Analysis--Each extract was analyzed by GC/MS in a Hewlett-Packard Model 5982 or a Hewlett-Packard Model 5985 GC/MS computer system. Both capillary and packed column gas chromatography were used.

Chromatographic peaks were identified by analysis of individual mass spectra. The three techniques used were:

- Manual interpretation of an unknown mass spectrum.

- Comparison of the unknown mass spectrum against the mass spectrum generated from the analysis of a previously analyzed standard.

- Computer search of the unknown mass spectrum against libraries containing reference spectra.

Selected ion current profile (SICP) searches were used to identify trace levels of selected organic species. This technique is based on the appearance of key ions within a narrow retention time window. It was used primarily to search for polynuclear aromatic hydrocarbons in the extracts.

Details of the analyses of the extracts are given in Appendix A (Volume 2).

4.4.2 Semi-Quantitative Organic Analyses

Semi-quantitative analyses of the identified compounds were achieved by measurement of the area under the selected ion current profile for each compound. For a given compound, the area under the most abundant ion was calculated with the use of the data system. The computed area was then compared to the area found for the most abundant ion of the appropriate internal standard, d_{10}-anthracene or d_8-toluene.

Radian determined for many compounds the response factors relative to d_{10}-anthracene and d_8-toluene. A value of 1.0 was used when the response factor was not known.

Electron impact (70 eV) ionization was used exclusively for analyses. The mass spectral information obtained was stored on magnetic discs for future interpretation and reference.

4.5 Quality Control

Numerous procedures were used to insure the quality of the data obtained. Both accuracy and precision were considered vital to the success of the program.

4.5.1 Screening

The Bacharach Instrument Company J-W Model TLV Sniffer was considered to be a reliable instrument for the screening of baggable sources. To insure that all screening results were obtained on an equivalent basis, the procedures listed below were followed.

- The battery pack for the instrument was fully recharged each night.

- The instrument and the dilution probe were calibrated before the start of each sampling day. Each concentration range on the instrument was calibrated separately.

- The instrument was allowed to warm up for ten minutes before screening began.

- The meter was zeroed before each screening.

- The meter was always held in an upright position; meter position affects the distribution of heat in the catalytic element.

- The small orifice in the dilution probe, the small diameter extension and the cotton filter chamber sections of the probe were inspected and cleaned frequently.

The TLV Sniffer was calibrated with several hexane-air standards according to the procedure described in Appendix A (Volume 2).

4.5.2 Sampling

Several procedures were followed to assure that baggable samples were representative of their sources:

- Mylar and Tedlar plastics were used as sample bags because they do not adsorb hydrocarbons.
- A cold trap in the sampling train trapped water and hydrocarbons to prevent condensation in downstream equipment. The contents of the cold trap were measured and the values recorded.
- Tent enclosures were kept as small as possible to minimize or prevent condensation in downstream equipment. The contents of the cold trap were measured and the values recorded.
- Tent enclosures were kept as small as possible to minimize or prevent condensation of heavy hydrocarbons. Tents were sealed securely.
- Sampling was not begun until equilibrium was established throughout the sampling system. The

TLV Sniffer was used to indicate that equilibrium
had been established.

Duplicate samples were taken whenever practical. Particular care was given to the care of grab samples for fixed gases (CO_2, N_2, H_2, O_2 and CO), hydrocarbons, gaseous sulfur species, and NO_x analyses. If analysis could not begin within 15 minutes of capture, a new sample was obtained. These samples were also dried and particulates were removed to help preserve their integrity.

4.5.3 On-Site Analyses

Approved analysis methods were followed. All instruments were calibrated frequently with approved standards. Duplicate analyses were made on many samples; titrations were repeated until reproducible results were obtained. Blanks were used whenever specified in a procedure, as were standard curves.

The organics in water samples were purged from the samples into a Teflon sample bag for analysis with the THC analyzer. This bag was thoroughly flushed with zero grade nitrogen between samples and a blank sample analyzed for THC at the end of each flushing.

A "zero carbon" water standard was prepared by Radian for the TOC analyses. This standard was considered superior to commercial standards. Several TOC analyses were made for each sample because the analysis sample is so small that it is difficult to obtain a single representative portion.

4.5.4 Species Identification

Special precautions were required in the preparation of samples for determination of trace organic species. Only high-purity distilled-in-glass solvents (Burdick and Jackson) were used. Only Teflon, glass, or stainless steel labware contacted the samples. All laboratory glassware was cleaned with chromic acid and, immediately before use, rinsed with an organic solvent to remove any traces of organic material. Aqueous reagents were presaturated with solvent before use.

As with other procedures in this program, only accepted and approved methods were used.

5.0 RESULTS OF REFINERY MEASUREMENTS AND SURVEYS

The results of measurements of atmospheric emissions at 13 petroleum refineries are summarized in this section of the report. Emission data were obtained from baggable sources (valves, flanges, pump seals, compressor seals, drains, and relief valves), nonbaggable sources (cooling towers and wastewater treating units), and process stacks. Also included in this section are summaries of the species identification results and the results of the quality control activities. The refinery survey results are also discussed. A more comprehensive presentation of the measurement data and results is given in Appendix B (Volume 3). The statistical treatment of the data is discussed in detail in Appendix C (Volume 4).

5.1 Baggable Source Measurements and Results

As previously described in Section 4 and in Appendix A (Volume 2), all baggable sources were chosen on the basis of choice variables and were selected in each refinery from process flow diagrams. The screening and emissions measurement results, the statistical model development, the valve maintenance study results and the distribution of baggable sources in refinery units are presented below.

5.1.1 Screening of Baggable Sources

The "screening values" refer to the maximum hydrocarbon concentration detected at selected baggable sources using the Bacharach TLV Sniffer calibrated with hexane. These screening values are expressed as ppmv of hydrocarbon. The results of screening baggable sources are presented in this section. It was found that the emissions sources were most conveniently grouped into twelve categories for analyses, presentation of results, and emission factor development. These twelve categories are given in Table 5-1. The total number of sources which were screened in each baggable source category are also presented in Table 5-1.

TABLE 5-1. CATEGORIES OF BAGGABLE SOURCES

Category	Source Description	Number of Sources Screened
1	Valves, Gas/Vapor Streams	563
2	Valves, Light Liquid/Two-Phase Streams	913
3	Valves, Heavy Liquid Streams	485
4	Valves, Predominantly Hydrogen Streams	135
5	Open-ended Lines (all streams)	129
6	Pump Seals, Light Liquid Streams	470
7	Pump Seals, Heavy Liquid Streams	292
8	Compressor Seals, Hydrocarbon Service	142
9	Compressor Seals, Hydrogen Service	83
10	Flanges (all streams)	2094
11	Drains (all streams)	257
12	Relief Valves (venting to atmosphere)	148

The volatility of the process streams associated with each of the baggable source types was found to have a significant effect on the frequency and rate of hydrocarbon emissions. Three hydrocarbon stream classifications were developed: gas/vapor streams, light liquid streams, and heavy liquid streams. The "gas/vapor" group contains those hydrocarbons which are completely vaporized at the process conditions. Light hydrocarbon liquids with boiling points below that of kerosene are included in the "light liquid" category. This group contains material having a vapor pressure above 0.1 psia at 100°F.

Hydrocarbon liquids with boiling points equivalent to or above that of kerosene are classified as "heavy liquid" streams. Those liquids with vapor pressures equal to or below 0.1 psia at 100°F fall into this classification. As a general rule, the most volatile stream component (or mixture of components) present at a concentration of 20 percent or more determines the stream classification.

The results of the screening activity are summarized in Table 5-2. The number and percentage of sources found to have a maximum screening value of 200 ppmv or greater are given. A Bacharach TLV Sniffer calibrated with hexane was used as the screening device. Both the screening instrument and the techniques are described in Section 4 of this document.

The 95 percent confidence interval for the percentage of sources screening $\geqslant$ 200 ppmv is also presented for each of the source categores. If all the sources in each category in refinery service could be screened, the percentage of sources found to screen $\geqslant$ 200 ppmv could be expected to fall between the given upper and lower boundaries 95 percent of the time.

The distribution of maximum screening values among screened baggable sources are presented in Table 5-3. They are given as functions of source types and process stream classification.

TABLE 5-2. SUMMARY STATISTICS FOR SCREENING OF BAGGABLE SOURCES

Source Type	Number Screened	Number Screening ⩾ 200 ppmv	Percent Screening ⩾ 200 ppmv	95% Confidence Interval for Percent Screening ⩾ 200 ppmv
Valves				
Gas-Vapor Streams	563	154	27.4	(24, 31)
Light Liquid/Two-Phase	913	330	36.1	(33, 39)
Heavy Liquid	485	32	6.6	(4, 9)
Hydrogen	135	59	43.7	(35, 52)
Open-Ended Valves	129	30	23.3	(16, 31)
Pump Seals				
Light Liquid Streams	470	296	63.0	(59, 67)
Heavy LIquid Streams	292	66	22.6	(18, 27)
Drains	257	49	19.1	(14, 24)
Flanges	2094	62	3.0	(2, 4)
Relief Valves	148	58	39.2	(31, 47)
Compressor Seals				
Hydrocarbon Service	142	102	71.8	(64, 79)
Hydrogen Service	83	69	83.1	(75, 91)

TABLE 5-3. DISTRIBUTION OF MAXIMUM SCREENING VALUES AMONG SCREENED SOURCES

Screening Range (ppmv)	Screened Sources Within Range Number	Screened Sources Within Range Percent
Valves - Gas/Vapor Streams		
Missing[a]	1	0.2
0	278	49.3
1-200	134	23.8
201-1000	33	5.8
1001-10,000	47	8.3
>10,000	71	12.6
	564	100%
Valves - Light Liquid/Two-Phase Streams		
Missing[a]	1	0.1
0	386	42.2
1-200	211	23.1
201-1000	70	7.7
1001-10,000	142	15.5
>10,000	104	11.4
	914	100%
Valves - Heavy Liquid Streams		
0	335	69.1
1-200	121	25.0
201-1000	21	4.3
1001-10,000	7	1.4
>10,000	1	0.2
	485	100%
Valves - Hydrogen Service		
0	47	34.8
1-200	30	22.2
201-1000	8	5.9
1001-10,000	22	16.3
>10,000	28	20.8
	135	100%

Continued

Table 5-3. Continued

Screening Range (ppmv)	Screened Sources Within Range Number	Percent
Valves - Open-Ended (All Streams)		
0	74	57.4
1-200	26	20.2
201-1000	7	5.4
1001-10,000	12	9.3
>10,000	10	7.7
	129	100%
Flanges (All Streams)		
Missing[a]	64	3.1
0	1748	83.5
1-200	225	10.7
201-1000	29	1.4
1001-10,000	17	0.8
>10,000	11	0.5
	2094	100%
Pump Seals - Light Liquid Streams		
0	67	14.3
1-200	107	22.8
201-1000	79	16.8
1001-10,000	104	22.1
>10,000	113	24.0
	470	100%
Pump Seals - Heavy Liquid Streams		
0	114	39.0
1-200	115	39.4
201-1000	24	8.2
1001-10,000	28	9.6
>10,000	11	3.8
	292	100%

Continued

TABLE 5-3. Continued

Screening Range (ppmv)	Screened Sources Within Range Number	Percent
Compressor Seals - Hydrocarbon Service		
Missing[a]	16	11.3
0	23	16.2
1-200	7	4.9
201-1000	11	7.7
1001-10,000	13	9.2
>10,000	72	50.7
	142	100%
Compressor Seals - Hydrogen Service		
Missing[a]	9	10.9
0	8	9.6
1-200	8	9.6
201-1000	8	9.6
1001-10,000	17	20.5
>10,000	33	39.8
	83	100%
Drains (All Streams)		
Missing[a]	2	0.8
0	138	53.7
1-200	73	28.4
201-1000	18	7.0
1001-10,000	14	5.4
>10,000	12	4.7
	257	100%
Relief Valves (All Streams)		
Missing[b]	112	44.4
0	61	24.2
1-200	33	13.1
201-1000	11	4.4
1001-10,000	23	9.1
>10,000	12	4.8
	252	100%

[a] Missing TLV value - screening data are not available.

[b] Relief valves selected, but not venting to the atmosphere, were not screened or sampled.

The screening values are not evenly distributed. For almost every source and stream category, the majority of the sources have screening values of 1000 ppmv or less (the only exceptions being compressor seal screening values). The skewness of the screening results is even more evident when the data are presented in graphical form. An example is Figure 5-1, where the distribution of screening values is shown for valves in light liquid stream service. The apparent "spike" at 10,000 ppmv was due to the limitations of the screening instrument. The Bacharach TLV Sniffer has an upper detection limit of 10,000 ppmv. A dilution probe allows this limit to be extended to 100,000 ppmv. However, this dilution probe was not used in the early stages of this study. Thus, all sources which screened above 10,000 ppmv were given a screening value of 10,000 during this period.

5.1.2 Hydrocarbon Emissions from Baggable Sources

Nonmethane hydrocarbon emissions from baggable sources were measured. Results and correlations of emission rates with process and equipment variables are discussed in this section of the report.

5.1.2.1 Distribution of Hydrocarbon Emission Rates

The results of the baggable source emissions sampling are summarized in Table 5-4. The distribution of nonmethane hydrocarbon leak rates among leak rate ranges is shown for the various source and process stream categories. As with the screening values, the emissions data are highly skewed for all sources. It is obvious from Table 5-4 that the bulk of emissions emanate from a small percentage of the fittings. For example, 76 percent of the total measured emissions from valves in light liquid/two-phase streams came from 3.5 percent of screened sources (or 9.7 percent of the leaking sources). This distribution is clearly illustrated in Figure 5-2 for nonmethane hydrocarbon emissions from valves in light liquid/two-phase stream service.

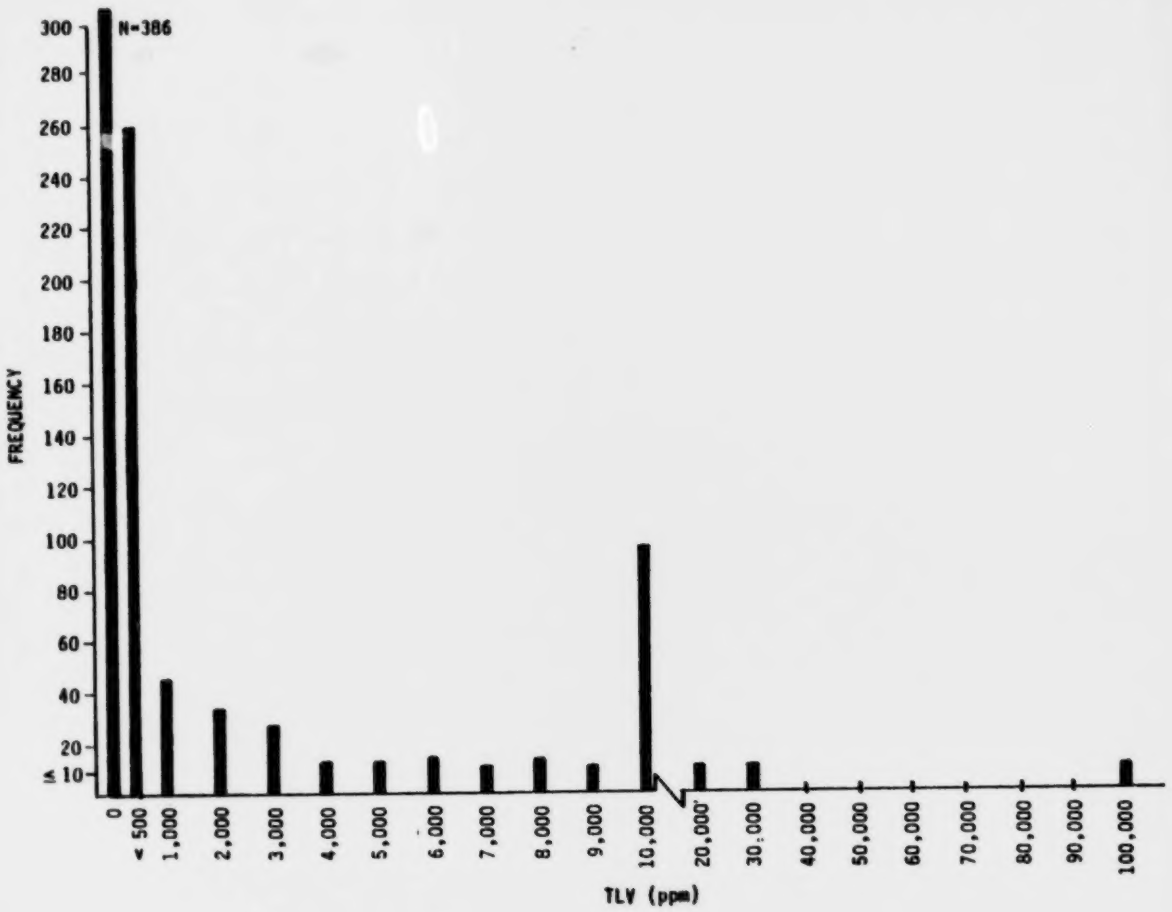


Figure 5-1. Distribution of Screening Values for Valves - Light Liquid Streams

TABLE 5-4. DISTRIBUTION OF NONMETHANE LEAK RATES FROM SAMPLED SOURCES

	Leaking Sources Within Range			Total Leakage Within Range	
Leak Range (lb/hr)	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
	Valves, Gas/Vapor Streams = 563 Screened				
>1.0	7	4.6	1.2	17.7654	70.0
0.1 - 1.0	18	11.7	3.2	5.9187	23.3
0.01 - .1	43	27.9	7.6	1.4867	5.9
0.001 - 0.01	49	31.8	8.7	0.2052	0.8
0.00001 - 0.001	37	24.0	6.6	0.0133	0.1
	154	100%	20.3%	25.3893	100%
	Valves, Light Liquid/Two-Phase Streams = 913 Screened				
>1.0	1	0.3	0.1	2.2297	14.4
0.1 - 1.0	31	9.4	3.4	9.3351	60.3
0.01 - .1	105	31.8	11.5	3.3877	21.9
0.001 - 0.01	121	36.7	13.3	0.5028	3.2
0.00001 - 0.001	72	21.8	7.8	0.0266	0.2
	330	100%	36.1%	15.4819	100%
	Valves, Heavy Liquid Streams = 485 Screened				
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	0	0.0	0.0	0.0	0.0
0.01 - .1	5	15.6	1.0	0.1773	74.1
0.001 - 0.01	13	40.6	2.7	0.0569	23.8
0.00001 - 0.001	14	43.8	2.9	0.0051	2.1
	32	100%	6.6%	0.2393	100%

Continued

TABLE 5-4. Continued

	Leaking Sources Within Range			Total Leakage Within Range	
Leak Range (lb/hr)	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Valves, Predominantly Hydrogen Streams = 135 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	3	5.1	2.2	0.3789	34.2
0.01 - .1	19	32.2	14.1	0.6691	60.4
0.001 - 0.01	18	30.5	13.3	0.0532	4.8
0.00001 - 0.001	19	32.2	14.1	0.0059	0.6
	59	100%	43.7%	1.1071	100%
Open-Ended Lines, All Streams = 129 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	1	3.3	0.8	0.1242	23.3
0.01 - .1	9	30.0	7.0	0.3475	65.3
0.001 - 0.01	12	40.0	9.3	0.0576	10.8
0.00001 - 0.001	8	26.7	6.2	0.0033	0.6
	30	100%	23.3%	0.5326	100%
Flanges = 2094 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	4	6.4	0.19	0.8655	63.2
0.01 - .1	12	19.4	0.57	0.4117	30.1
0.001 - 0.01	28	45.2	1.33	0.0820	6.0
0.00001 - 0.001	18	29.0	0.86	0.0096	0.7
	62	100%	2.95%	1.3688	100%

Continued

TABLE 5-4. Continued

	Leaking Sources Within Range			Total Leakage Within Range	
Leak Range (lb/hr)	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
		Pump Seals, Light Liquid Streams = 470 Screened			
>1.0	19	6.4	4.0	63.1913	70.6
0.1 - 1.0	73	24.7	15.5	22.0347	24.6
0.01 - .1	107	36.1	22.7	3.9430	4.4
0.001 - 0.01	77	26.0	16.4	0.3274	0.4
0.00001 - 0.001	20	6.8	4.3	0.0086	0.0
	296	100%	62.9%	89.5051	100%
		Pump Seals, Heavy Liquid Streams = 292 Screened			
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	16	24.2	5.5	4.3189	73.2
0.01 - .1	28	42.4	9.6	1.5089	25.6
0.001 - 0.01	17	25.8	5.8	0.0699	1.2
0.00001 - 0.001	5	7.6	1.7	0.00178	0.0
	66	100%	22.6%	5.8995	100%
		Drains = 257 Screened			
>1.0	4	8.2	1.6	7.3958	61.6
0.1 - 1.0	12	24.5	4.7	3.9615	33.0
0.01 - .1	17	34.7	6.6	0.5939	4.9
0.001 - 0.01	13	26.5	5.1	0.0630	0.5
0.00001 - 0.001	3	6.1	1.1	0.0013	0.0
	49	100%	19.1%	12.0155	100%

Continued

TABLE 5-4. Continued

Leak Range (lb/hr)	Leaking Sources Within Range			Total Leakage Within Range	
	No.	% of Leaking Sources	% of Total Sources Screened	Total Leakage (lb/hr)	% of Total Source of Leakage
Relief Valves = 148 Screened					
>1.0	5	8.6	3.4	15.5383	76.0
0.1 - 1.0	15	25.9	10.1	3.9313	19.2
0.01 - .1	22	37.9	14.7	0.9121	4.5
0.001 - 0.01	12	20.7	8.1	0.0580	0.3
0.00001 - 0.001	4	6.9	2.7	0.0022	0.0
	58	100%	39.0 %	20.4419	100%
Compressor Seals, Hydrocarbon Service = 142 Screened					
>1.0	23	21.9	16.2	67.9440	74.3
0.1 - 1.0	48	45.7	33.8	22.2482	24.3
0.01 - .1	24	22.9	16.9	1.3014	1.4
0.001 - 0.01	7	6.6	4.9	0.0224	0.0
0.00001 - 0.001	3	2.9	2.1	0.0013	0.0
	105	100%	73.9 %	91.5172	100%
Compressor Seals, Hydrogen Service = 83 Screened					
>1.0	0	0.0	0.0	0.0	0.0
0.1 - 1.0	14	20.3	16.9	3.3954	75.6
0.01 - .1	22	31.9	26.5	1.0105	22.5
0.001 - 0.01	21	30.4	25.3	0.0794	1.8
0.00001 - 0.001	12	17.4	14.5	0.0064	0.1
	69	100%	83.2	4.4917	100%

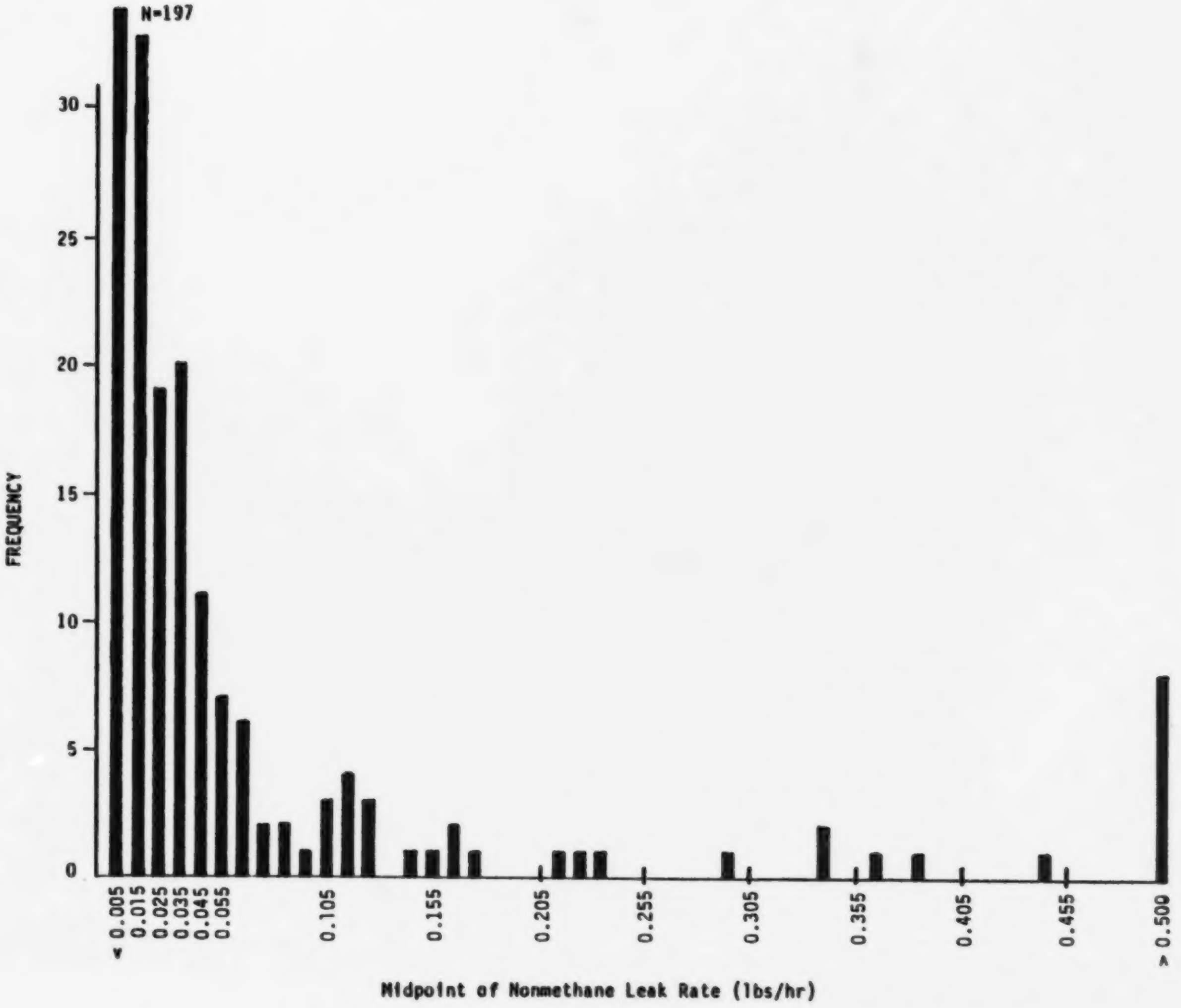


Figure 5-2. Distribution of Leak Rates for Valves - Light Liquid/Two-Phase Streams.

The frequency distributions of the screening values and the leak rates are similarly skewed. This suggested a possible correlation between the leak rates and screening values for the various baggable sources. Such correlations were found to exist, and they are presented in the form of nomographs in Section 5.1.3 of this report.

5.1.2.2 Statistical Treatment of Baggable Source Emission Data

The high degree of skewness in the distribution of nonmethane leak rates from baggable sources precluded a conventional statistical treatment of the data. In addition to the skewness, a large percentage of the studied sources were considered "non-leaking." The efficient estimation of emission factors and their variances, as well as the inclusion of non-leaking sources, required the development and use of sophisticated statistical procedures.

A lognormal distribution was used to model the distribution of leaking sources. This distribution has the property that when the original data are transformed by taking natural logarithms, the transformed data will follow a normal distribution. The lognormal distribution is often appropriate when the standard error of an individual value is proportional to the magnitude of the value. The form of the lognormal distribution is as follows:

$$f(x) = \frac{\exp\left[-\frac{(\ell n\ x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \qquad \text{for } 0 > x > \infty$$

$$= 0 \qquad \text{for } x \leqslant 0$$

$$\text{Mean} = \exp\left[\mu + \frac{2\sigma^2}{2}\right]$$

$$\text{Variance} = \exp[2\mu + 2\sigma^2] - \exp[2\mu + \sigma^2]$$

To develop estimates for emission factors, the nonleaking sources (leak rate assumed equal to zero) also had to be modeled. A mixed distribution, specifically a lognormal distribution with a discrete probability mass at zero, was used for this purpose. Letting ρ equal the fraction of nonleaking sources in the population, this mixed-lognormal distribution has the following form:

$$f(x) = \frac{(1 - \rho)\ \exp\left[-\frac{(\ell n\ x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} \qquad \text{for } 0 < x < \infty$$

$$= \rho \qquad \text{for } x = 0$$

$$= 0 \qquad \text{for } x < 0$$

$$\text{Mean} = (1 - \rho)\ \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = (1 - \rho)\ [\exp(2\mu + \sigma^2)]\ [\exp(\sigma^2) - (1 - \rho)]$$

Efficient estimates of the mean and variance of the population model by this mixed distribution have been developed.[23,24] These estimates are as follows.

The best unbiased estimator of the population mean emission rate is

$$m = \left[\left(1 - \frac{r}{n}\right)\exp\ [(\bar{x})]\ g\left(\frac{s^2}{2}\right)\right]$$

and the best unbiased estimator of the population variance of the emission rate is

$$v = \left(1 - \frac{r}{n}\right)\ \exp(2\bar{x})\ \left[g(2S^2) - \left(1 - \frac{r}{n - 1}\right)g\left(\frac{n - r - 2}{n - r - 1}\ s^2\right)\right]$$

where

n = number of sources screened

r = number of sources screened 200 ppm or with measured leak $< 10^{-5}$ lb/hr

$m = n - r$
$\quad$ = number of "leaking" sources

$g(t)$ = infinite series

$$= 1 + \frac{(m-1)t}{m} + \frac{(m-1)^3\ t^2}{m^2 2!\ (m+1)}$$

$$+ \frac{(m-1)^5\ t^3}{m^3 3!\ (m+1)(m+3)} \quad \ldots.$$

$\overline{x}$ = average of logarithm of leaking sources

$$= \sum_{1}^{n-r} \ell n\ (\text{nonmethane leaks})/(n-r)$$

s^2 = variance of the logarithm of leaking sources

$$= \sum_{1}^{n-r} [\ell n\ (\text{nonmethane leaks}) - \overline{x}\ ]^2/(n-r-1)$$

The mean and variance formulas hold whenever there is more than one leaking source ($n - r > 1$). When only one leaking source is identified, the following estimates are appropriate:

$$\text{mean} = \frac{x_1}{n} \text{ and variance} = \frac{x_1{}^2}{n}\ ,$$

where x is the single measured leak. If no leaks are found (r = n), then the best estimate for both the mean and variance is zero.

Computer programs were developed for these estimators and the estimator for the mean was used for all emission factors developed from the emissions data.

Data distributed lognormally can be transformed to a normal distribution by taking natural logarithms of the data. The distribution assumption for the leaking sources was tested by examining distributions of the log-leak rates. Histograms displaying these distributions were constructed for all important source type and process stream classifications. An example is shown in Figure 5-3. The data for most sources appeared to adequately approximate a normal distribution after the transformation.

To statistically test the assumption of a normal distribution for the log-leak rates, skewness and kurtosis statistics were computed for each data group and tested for departures from their expected values of zero in a normal distribution. Table 5-5 summarizes these statistics.

Only three of the twelve cases indicate significant lack of normality.

The development and refinement of the statistical procedures are presented in greater detail in Appendix C (Volume 4). The emission factors developed with these procedures are presented in the following section 5.1.2.3 of this report. Also presented in Section 5.1.2.3 are the effects of various equipment and process variables on leak rates and emission factors.

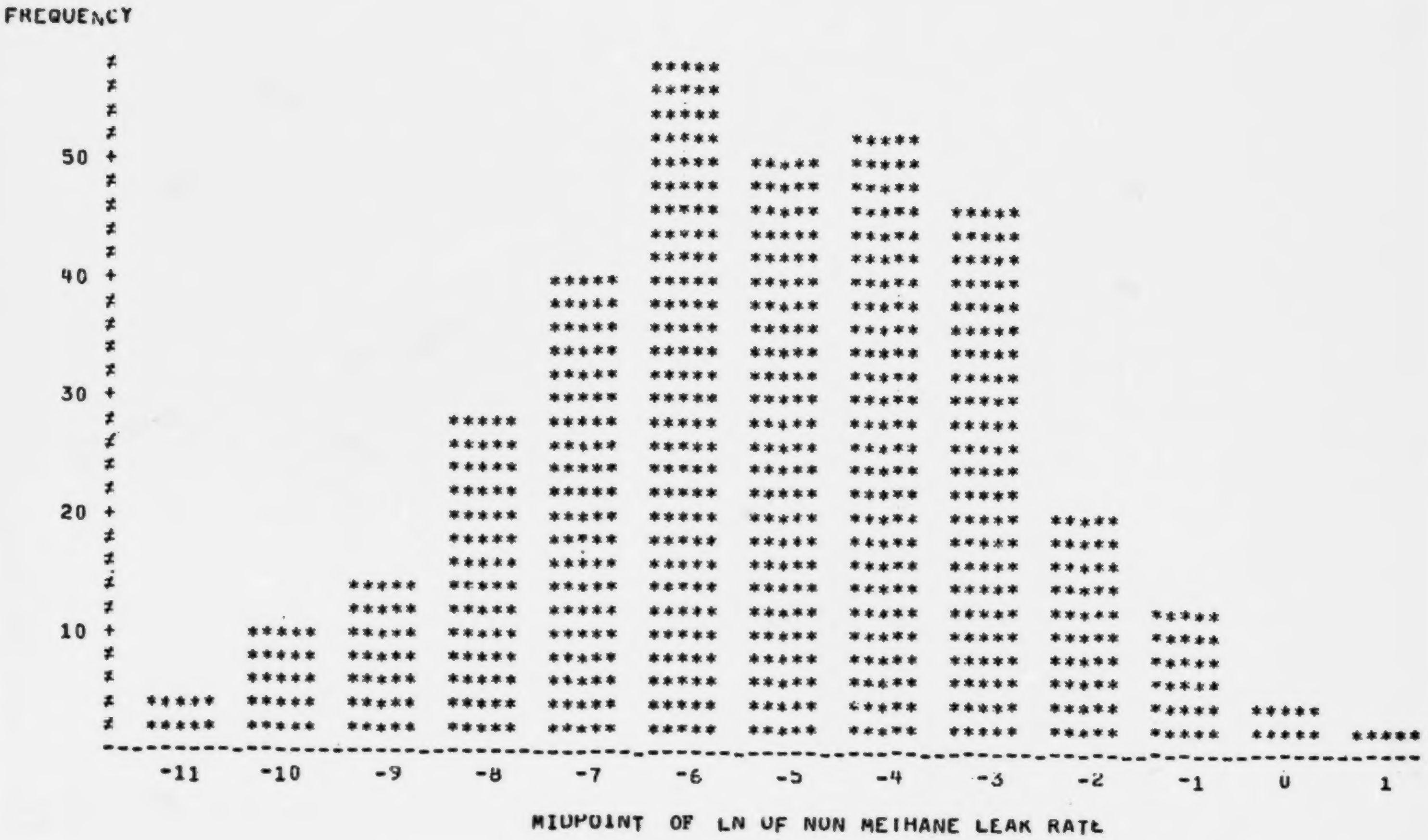


Figure 5-3. Histogram of LN of Nonmethane Leak Rate Valves - Light Liquids/Two-Phase Streams.

TABLE 5-5. SKEWNESS AND KURTOSIS STATISTICS

Source Type/ Stream Group	Number of Leaking Sources	Skewness	Kurtosis
Valves			
Gas/Vapor Streams	154	0.19	-0.33
Light Liquids/Two-Phase	330	-0.16	-0.18
Heavy Liquids	32	0.28	-0.88
Hydrogen Streams	59	-0.18	-1.09*
Open-ended Valves	30	-0.01	-0.98
Pump Seals [1]			
Light Liquids	296	0.03	-0.36
Heavy Liquids	66	-0.77*	0.06
Compressor Seals [2]			
Hydrocarbon Service	102	-0.99*	1.16*
Hydrocarbon Service	69	-0.29	0.69
Flanges	62	0.39	0.20
Drains	49	-0.04	-0.47
Relief Valves	58	-0.05	-0.21

* probability <.05 given a normal distribution.

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[1] All data needed to classify sources into stream type were not available for all pump seals and valves. Those particular sources are not included in this analysis.

[2] Compressor seals screening < 200 ppmv were not included in this analysis.

5.1.2.3 Emission Factors for Baggable Sources in Refineries

The estimated emission factors for nonmethane hydrocarbon emissions for the six types of baggable sources are summarized in Table 5-6. Twelve emission factors are presented representing the twelve categories of source type and process stream group. Confidence intervals are given in each case for the estimated emission factor. The confidence interval for the emission factors represents the range of values which is expected with 95 percent confidence to include the average emission rate for all sources of the particular type in all U. S. refineries. The confidence intervals include consideration of both potential biases and random variation as discussed in Appendix C (Volume 4).

The emission factors listed in Table 5-6 are slightly different than those published in a previous report (EPA 600/2-79-044).[25] The results given here are based on further refinements of the data base and the formation of emission factors for valves in hydrogen service which were previously incorporated in other valve service categories.

The effect of process variables on emission factors was investigated. Any discussion of the effect of process variables is complicated by the confounding between variables in the data base. This confounding is due to the lack of independence between process variables as they naturally occur. In addition, all combinations of levels of many variables could not be obtained in the study.

A fractional factorial experimental design was followed in selecting sources for screening and possible sampling. Selection was based on key process variables. The design allowed the estimation of the main effects of important variables, but not all variable interaction effects could be estimated. Most second order interactions (e.g., stream type by line size by source type) and higher order interactions are either confounded or there are not enough replicate data to quantify their effects with any precision.

TABLE 5-6. ESTIMATED VAPOR EMISSION FACTORS FOR NONMETHANE HYDROCARBONS FROM BAGGABLE SOURCES

Source Category	Emission Factor Estimate (lb/hr/source)[a]	95% Confidence Interval for Emission Factor (lb/hr/source)[b]
Valves		
Gas-Vapor Streams	0.059	(0.030, 0.110)
Light Liquid/Two-Phase	0.024	(0.017, 0.036)
Heavy Liquid	0.0005	(0.0002, 0.0015)
Hydrogen	0.018	(0.007, 0.045)
Open-Ended Lines	0.005	(0.0016, 0.016)
Pump Seals		
Light Liquid Streams	0.25	(0.16, 0.37)
Heavy Liquid Streams	0.046	(0.019, 0.11)
Drains	0.070	(0.023, 0.20)
Flanges	0.00056	(0.0002, 0.0025)
Relief Valves	0.19	(0.070, 0.49)
Compressor Seals		
Hydrocarbon Service	1.4	(0.66, 2.9)
Hydrogen Service	0.11	(0.05, 0.23)

[a] The estimated mean level of emissions from all sources of this type in United States refineries. This factor is an average and incorporates the fact that a significant number of sources have no emissions while others have emissions ranging from 10^{-3} to 10 lbs/hr.

[b] The statistical procedures used to construct those intervals account for both systematic and random errors in experimental design, sampling, chemical analysis, and statistical analysis. The procedures used are such that at least 95% of the intervals will include the time emission factor for a particular source category.

This means that it is difficult to break sources down by more than two variables at a time to determine emission factors or effects.

Emission factors and confidence intervals were developed for selected classifications of the baggable sources (such as seal types for pumps). The results are presented in Appendix B (Volume 3). Leak rates in any category span three or more orders of magnitude. Because of this phenomenon, it is impossible to precisely estimate the emission factors from the relatively small number of sources that were screened and sampled. The confidence intervals for the emission factors of selected classifications of sources are very wide, and overlap in most cases. Thus, any apparent differences between emission factors for the various categories of a source may not be real.

5.1.3 Relationships Between Screening Values and Leak Rates

The results of the baggable source screening and leak sampling program were analyzed. It was found that relationships exist between the screening values and the source leak rates.

Appendix C (Volume 4) of this report contains detailed descriptions of the statistical techniques and models developed to correlate the emissions data. Statistical analyses were performed to determine:

(a) The linear regression equations for each baggable source and stream type combination.

(b) The possibility of combining some of the equations found in (a) to reduce the total number of necessary equations.

A linear equation of the form below was proposed.

$$\log_{10} L = B_0 + B_1 \log_{10} M \qquad (5\text{-}1)$$

where

L = nonmethane hydrocarbon leak rate, lb/hr

B_0, B_1 = constants, intercept and slope respectively.

M = maximum screening (or rescreening) value, ppmv.

The regressions for each source type-process stream combination are given in Table 5-7.

Analyses of covariance were performed to determine which source and process stream types could be combined for prediction purposes. It was found that the source and stream types could be grouped such that seven equations were adequate for predicting leak rates from screened sources. The seven groups are as follows:

- Pumps in light liquid streams, compressors and relief valves in gas/vapor streams.
- Valves and compressor seals in hydrogen service.
- Valves in gas/vapor streams.
- Valves in light liquid/two-phase streams.
- Flanges.
- Drains.
- Pump seals in heavy liquid streams.

TABLE 5-7. REGRESSION OF LOG LEAK RATE ON LOG MAXIMUM RESCREENING VALUE BY SOURCE AND STREAM TYPE

Process Stream Type[a]		Valves	Flanges	Pump Seals	Compressor Seals	Drains	Relief Valves
Gas/Vapor	B_0	-7.04			-3.97		-4.41
	$SE(B_0)$	0.56			0.74		0.45
	B_1	1.23			0.71		0.87
	$SE(B_1)$	0.12			0.16		0.10
	R^2	0.57			0.23		0.58
	N	79			69		54
Light Liquid/ Two-Phase	B_0	-4.90	-2.93	-4.59		-2.38	
	$SE(B_0)$	0.22	1.01	0.32		1.64	
	B_1	0.80	0.22	0.89		0.60	
	$SE(B_1)$	0.06	0.31	0.08		0.55	
	R^2	0.63	0.05	0.48		0.10	
	N	119	12	136		13	
Hydrogen	B_0	-7.45			-5.30		
	$SE(B_0)$	0.90			0.72		
	B_1	1.14			0.72		
	$SE(B_1)$	0.20			0.36		
	R^2	0.51			0.24		
	N	32			15		
Heavy Liquid	B_0	-9.82		-3.08		-3.35	
	$SE(B_0)$	1.12		0.77		0.31	
	B_1	2.26		0.57		0.51	
	$SE(B_1)$	0.34		0.23		0.11	
	R^2	0.96		0.29		0.60	
	N	4		17		17	
Stream Information Missing	B_0	-5.68	-5.08	-4.77			
	$SE(B_0)$	0.54	0.88	1.50			
	B_1	0.95	0.89	0.70			
	$SE(B_1)$	0.17	0.24	0.45			
	R^2	0.75	0.78	0.13			
	N	21	6	18			

[a] $\log_{10}(\text{leak rate}) = B_0 + B_1 \log_{10}(\text{max rescreening value})$

$SE(B_0)$ = standard error of B_0

$SE(B_1)$ = standard error of B_1

N = number of data pairs

R^2 = coefficient of determination or correlation coefficient squared

The resulting seven equations are summarized in Table 5-8. Also included in this table are the correlation coefficients and the confidence intervals for the slope and intercept values. The equations were used to develop nomographs which relate the predicted leak rate to the screening values for the various source and stream types. These nomographs are shown in Figures 5-4(A & B) through 5-10(A & B). Each nomograph gives the predicted mean leak rate as a function of the maximum TLV Sniffer screening readings taken directly at the source of the leak.

Although the equations were developed on a logarithmic scale, the nomographs are shown on an arithmetic scale for ease in reading and interpolation.

The 90 percent confidence intervals shown on the nomographs are for the mean leak rate. They should not be confused with confidence intervals for individual leak rates for given screening values. There is a substantial difference between the two leak rates. The differences are illustrated in Table 5-9. For example, the mean leak rate for a valve (gas/vapor stream) with a screening value of 10,000 ppmv is predicted to be 0.038 lb/hr. Any single valve with this screening value would be expected to have a leak rate between 0.0019 and 0.75 lb/hr 90 percent of the time. On the other hand, a large number of valves with a screening value of 10,000 ppmv should have a mean leak rate falling between 0.025 and 0.057 lb/hr. There is an order-of-magnitude difference between the two types of confidence intervals. This difference can be seen clearly in Figure 5-11.

The results of the baggable source screening and sampling can be presented and displayed in other useful ways. Nomographs have been prepared relating screening values to the percentage of each source type expected to have screening values above any selected value. Other nomographs have been prepared relating screening values to the percentage of total mass emissions which can be expected from sources with screening values greater than any given value. A discussion of nomograph development is presented in Appendix C (Volume 4).

TABLE 5-8. CORRELATION OF SCREENING (OR RESCREENING) VALUES WITH LEAK RATES

Source and Stream Type Group	Number of Data Pairs	Correlation Coefficient, R	Constants for Linear Equation[a]		95 Percent Confidence Interval	
			Intercept, B_0	Slope, B_1	For Intercept	For Slope
Pump Seals (Light Liquid/Two Phase Streams), Compressors (Gas/Vapor Streams), and Relief Valves (Gas/Vapor)	259	0.68	- 4.4	0.83	(- 4.9, - 3.9)	(0.72, 0.94)
Valves and Compressor Seals (Hydrogen Streams)	47	0.67	- 7.0	1.06	(- 8.5, - 5.5)	(0.72, 1.40)
Valves (Gas/Vapor Streams)	79	0.76	- 7.0	1.23	(- 8.1, - 5.9)	(0.99, 1.47)
Valves (Light Liquid/Two-Phase Streams)	119	0.79	- 4.9	0.80	(- 5.3, - 4.5)	(0.69, 0.91)
Drains	61	0.68	- 4.9	1.10	(- 5.8, - 4.0)	(0.80, 1.40)
Flanges	52	0.77	- 5.2	0.88	(- 5.9, - 4.5)	(0.68, 1.08)
Pump Seals (Heavy Liquid Streams)	61	0.75	- 5.1	1.04	(- 5.8, - 4.3)	(0.80, 1.27)

[a] $\log_{10}$ [leak rate (lb/hr)] = $B_0 + B_1 \log_{10}$ [Screening or Rescreening value, ppmv]

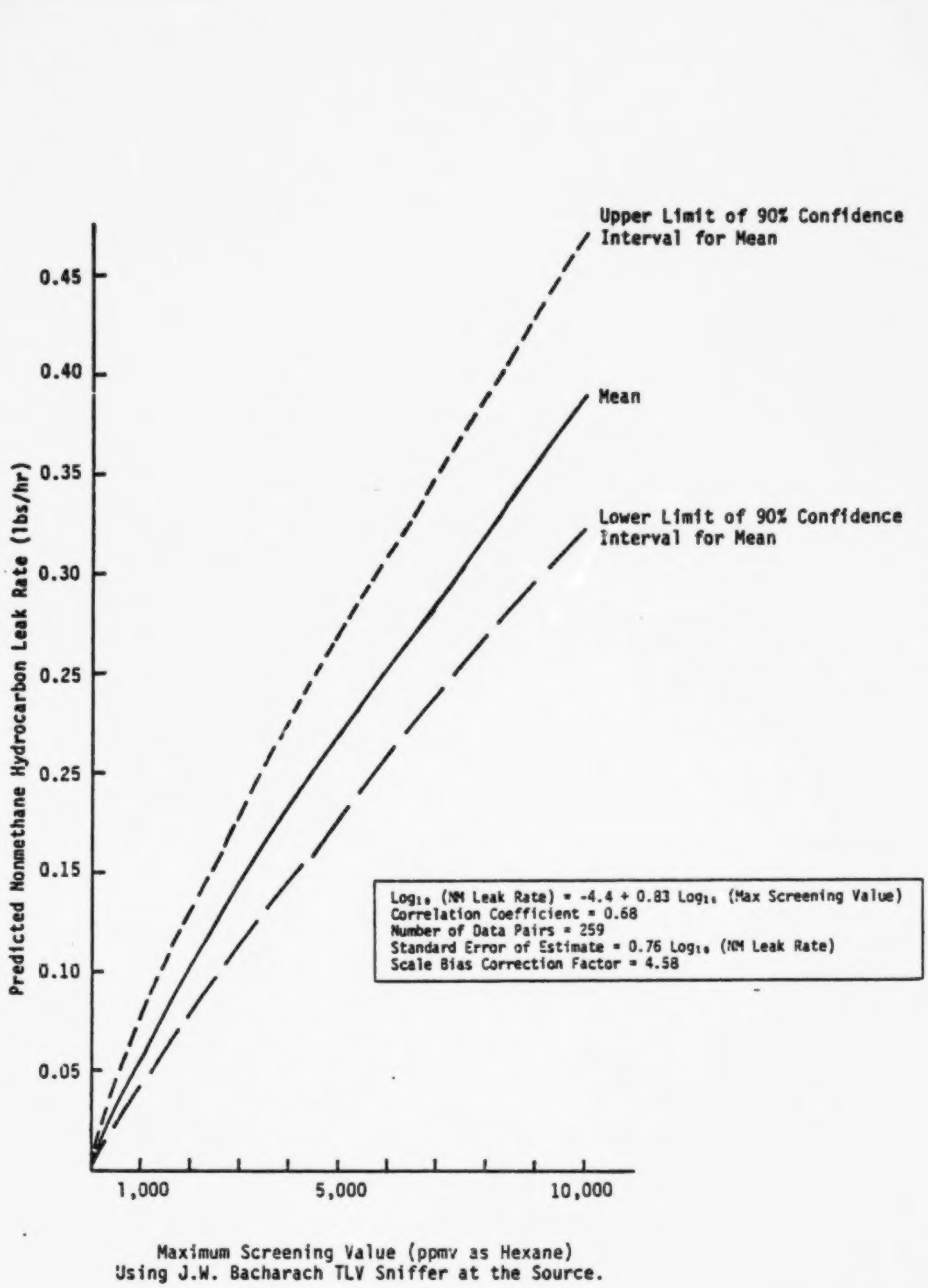


Figure 5-4A. Nomograph for Predicting Total Hydrocarbon Leak Rates from Maximum Screening Values - Pumps (light Liquids), Compressors, Relief Valves (Gas/Vapor Streams) (Part I: Screening values from 0 - 10,000 ppmv).

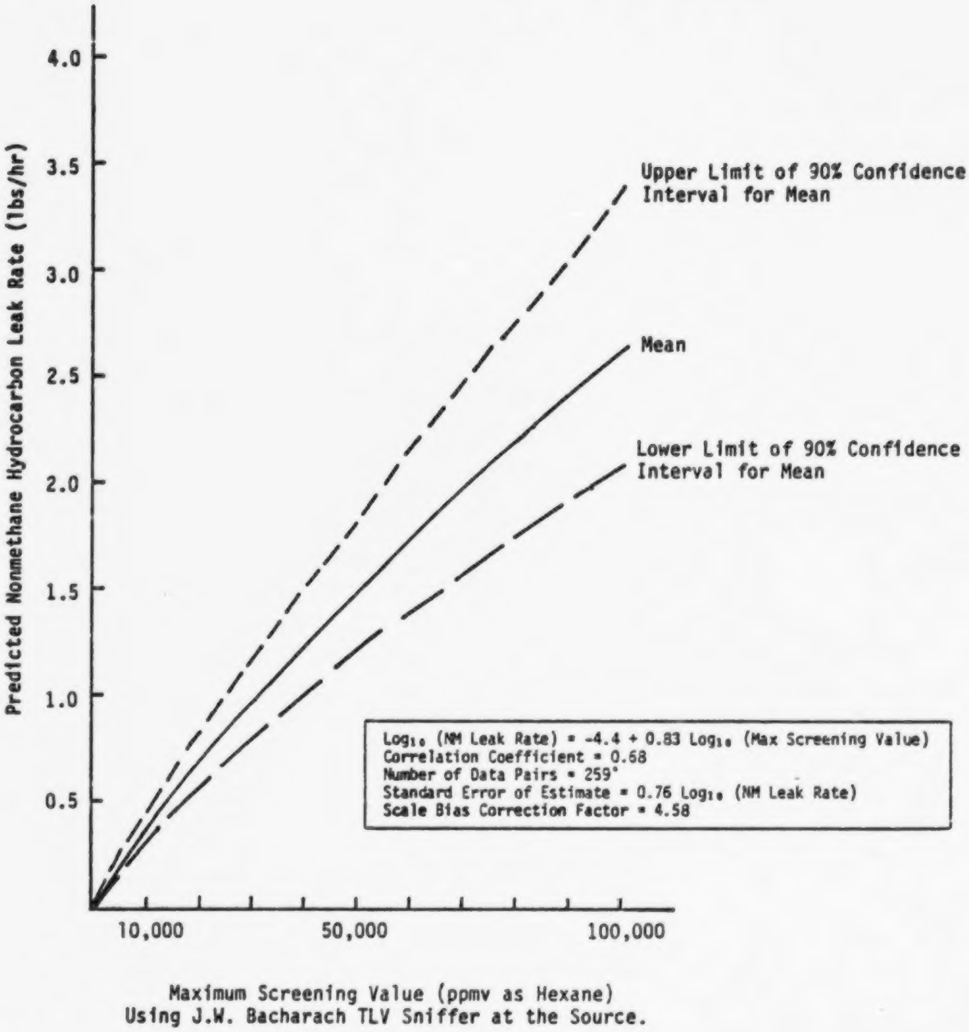


Figure 5-4B. Nomograph for Predicting Total Hydrocarbon Leak Rates from Maximum Screening Values - Pumps (Light Liquids), Compressors, Relief Valves (Gas/Vapor Streams) (Part II: Screening Values from 0 - 100,000 ppm).

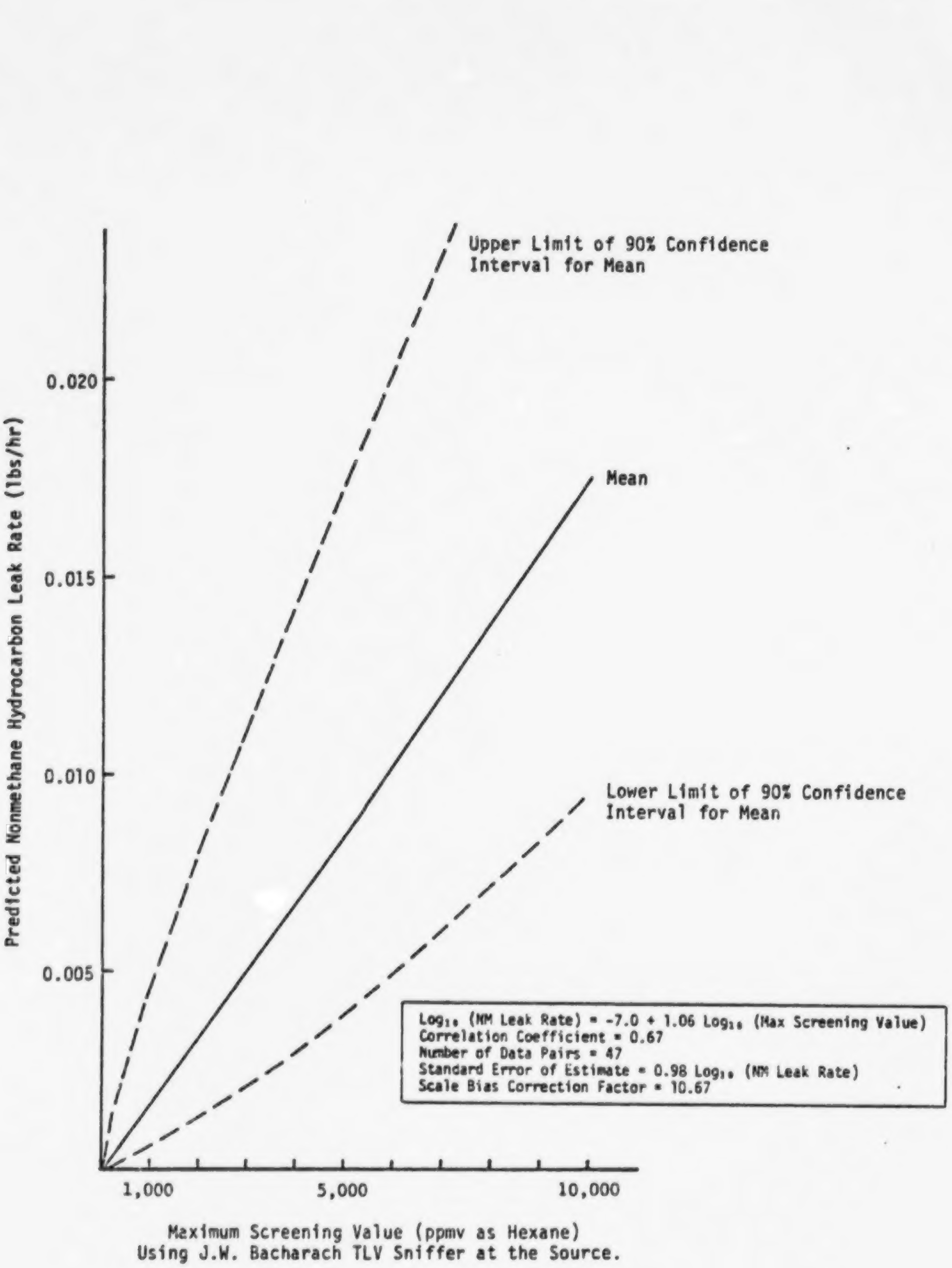


Figure 5-5A. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Compressors in Hydrogen Service (Part I: Screening Values from 0 - 10,000 ppm).

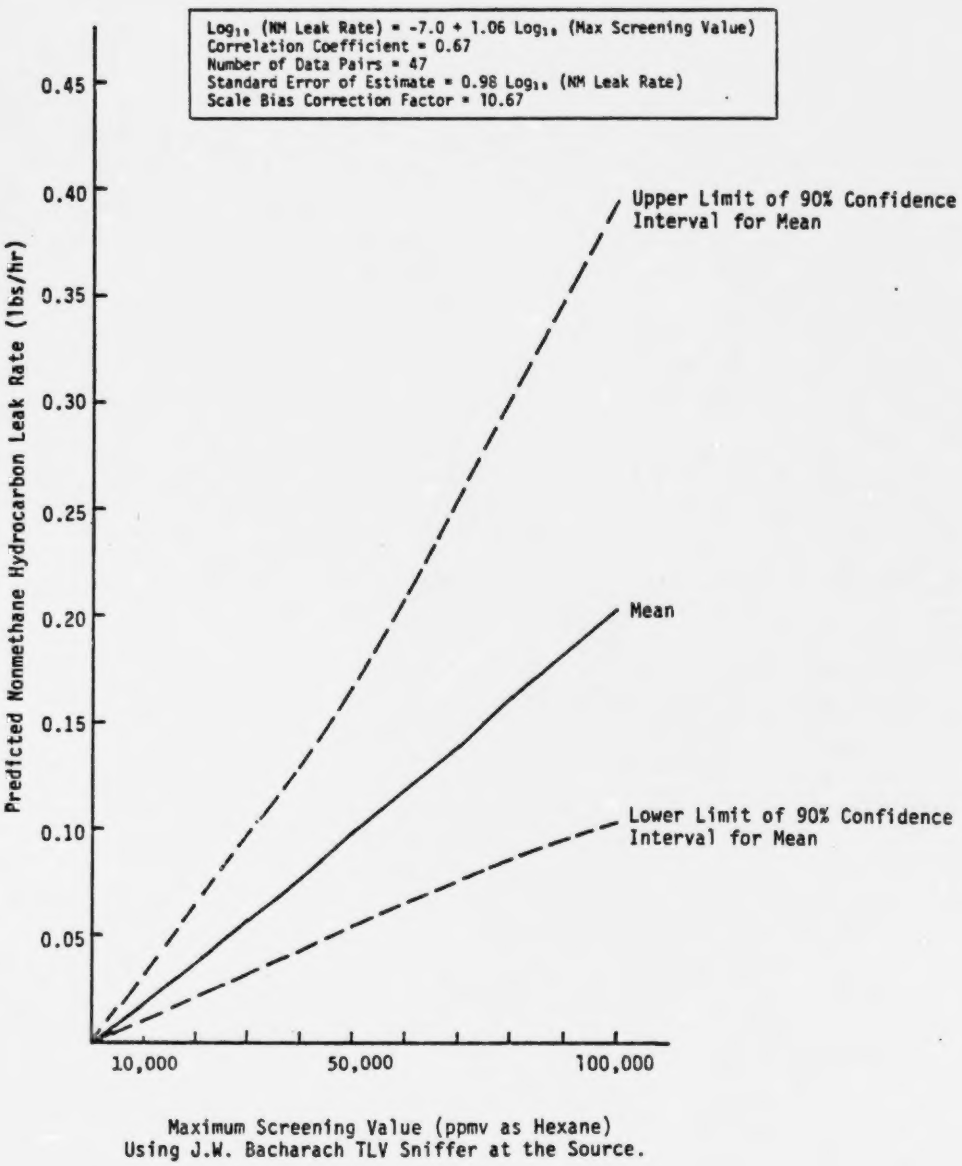


Figure 5-5B. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves and Compressors in Hydrogen Service (Part II: Screening Values from 0 - 100,000 ppm).

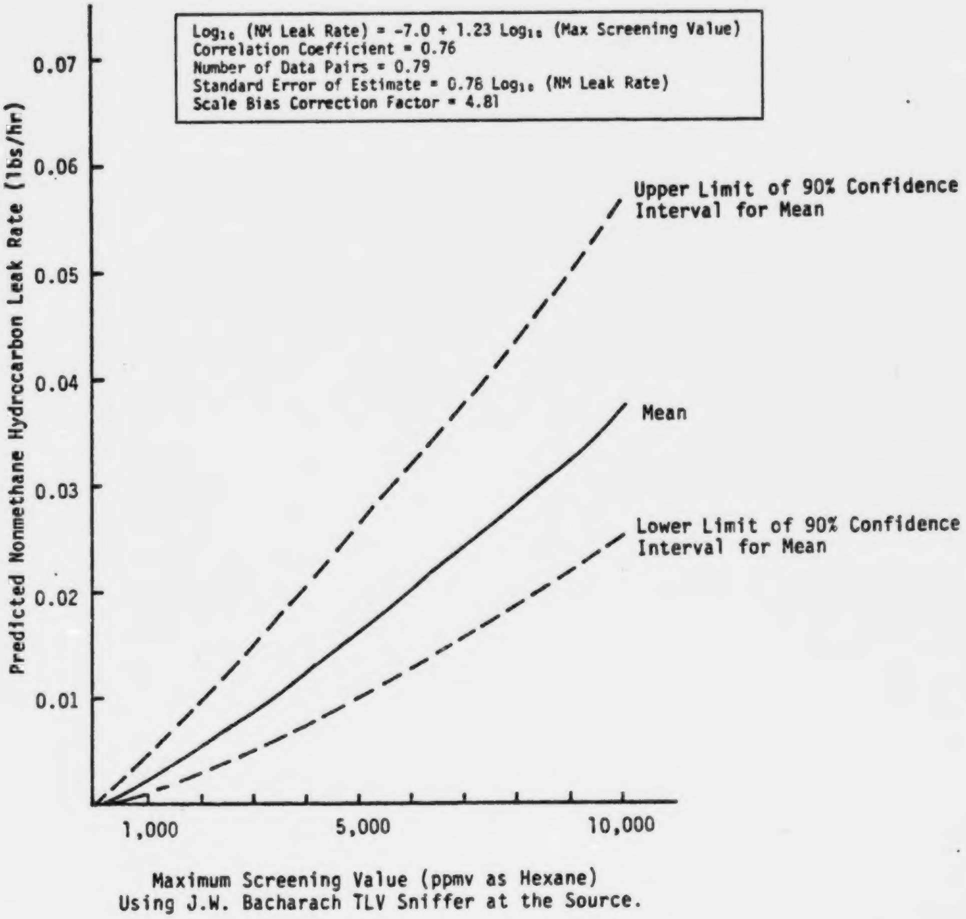


Figure 5-6A. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Gas/Vapor Streams (Part I: Screening Values from 0 - 10,000 ppm).

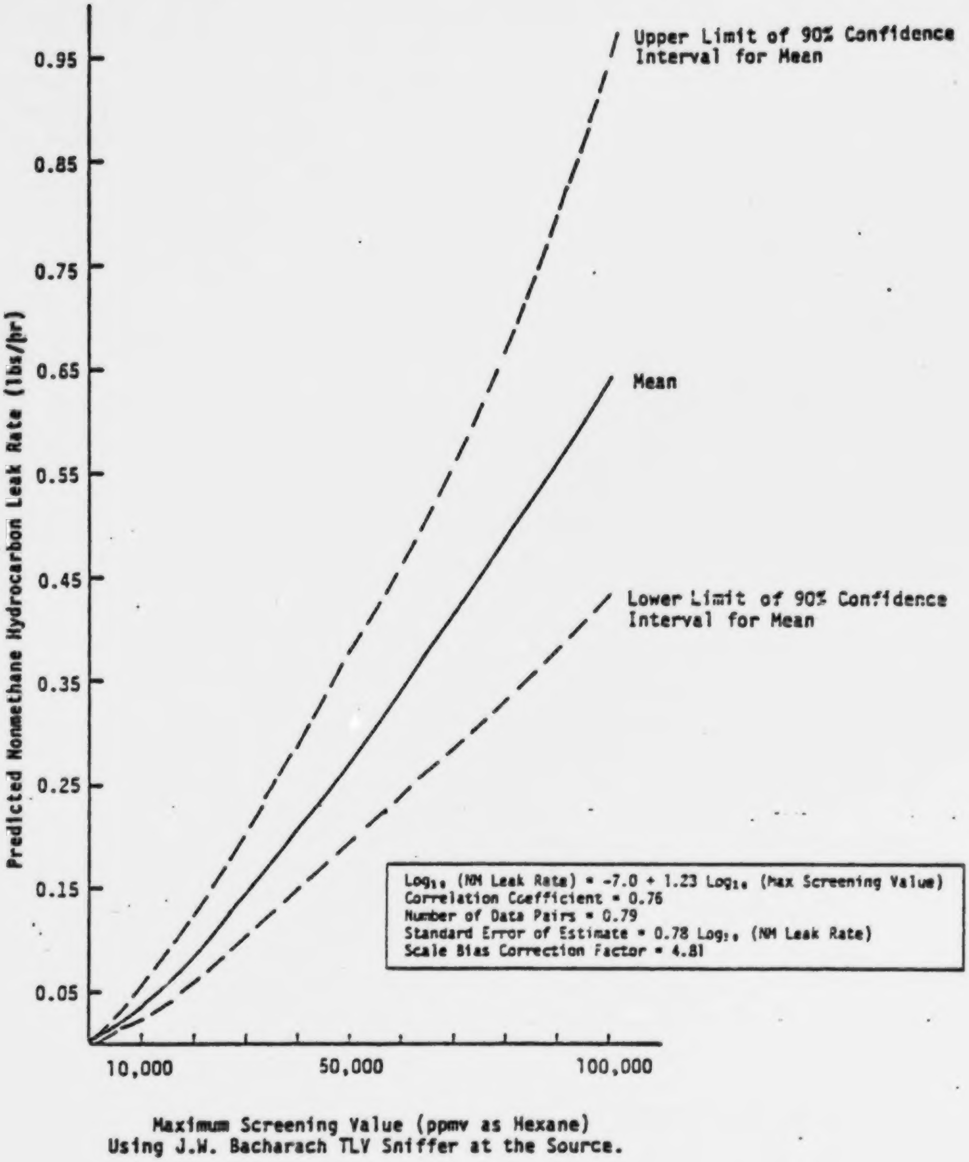


Figure 5-6B. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Gas/Vapor Streams (Part II: Screening Values from 0 - 100,000 ppm).

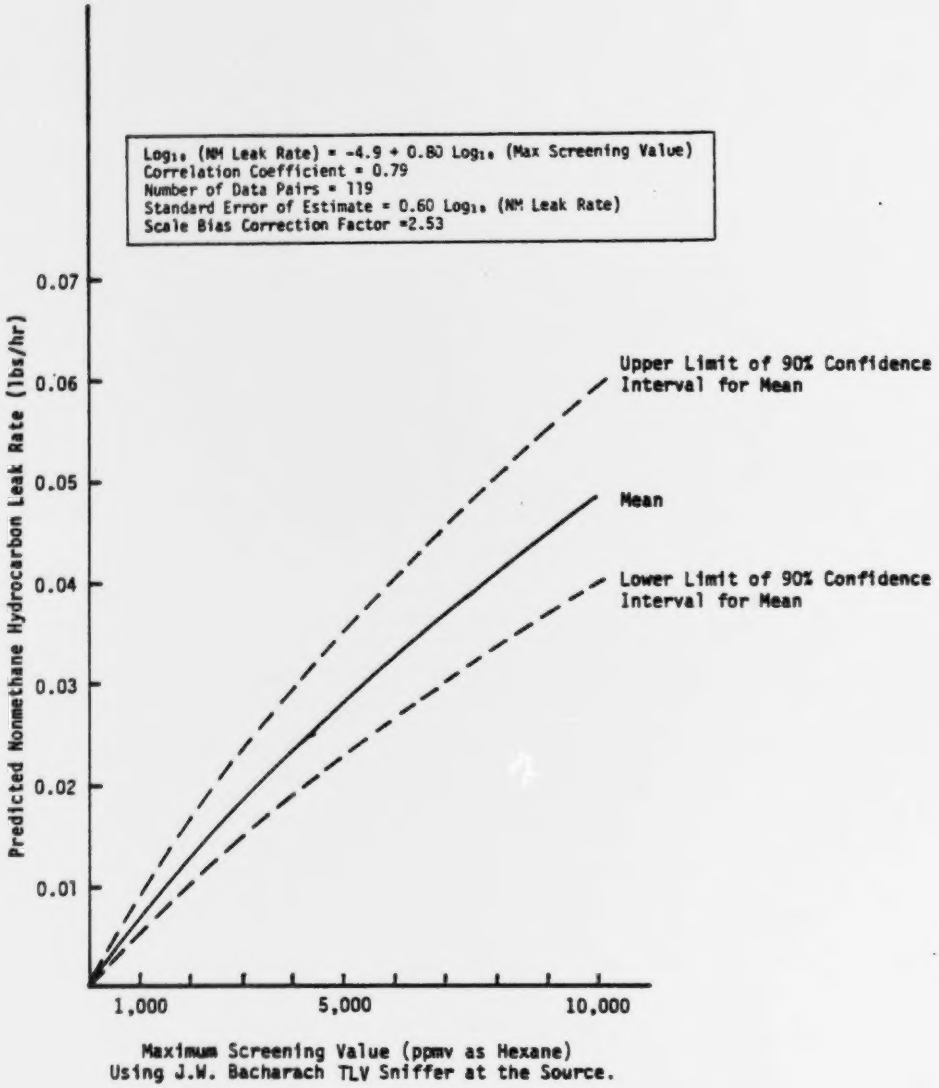


Figure 5-7A. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Light Liquid/Two-Phase Streams (Part I: Screening Values from 0 - 10,000 ppm).

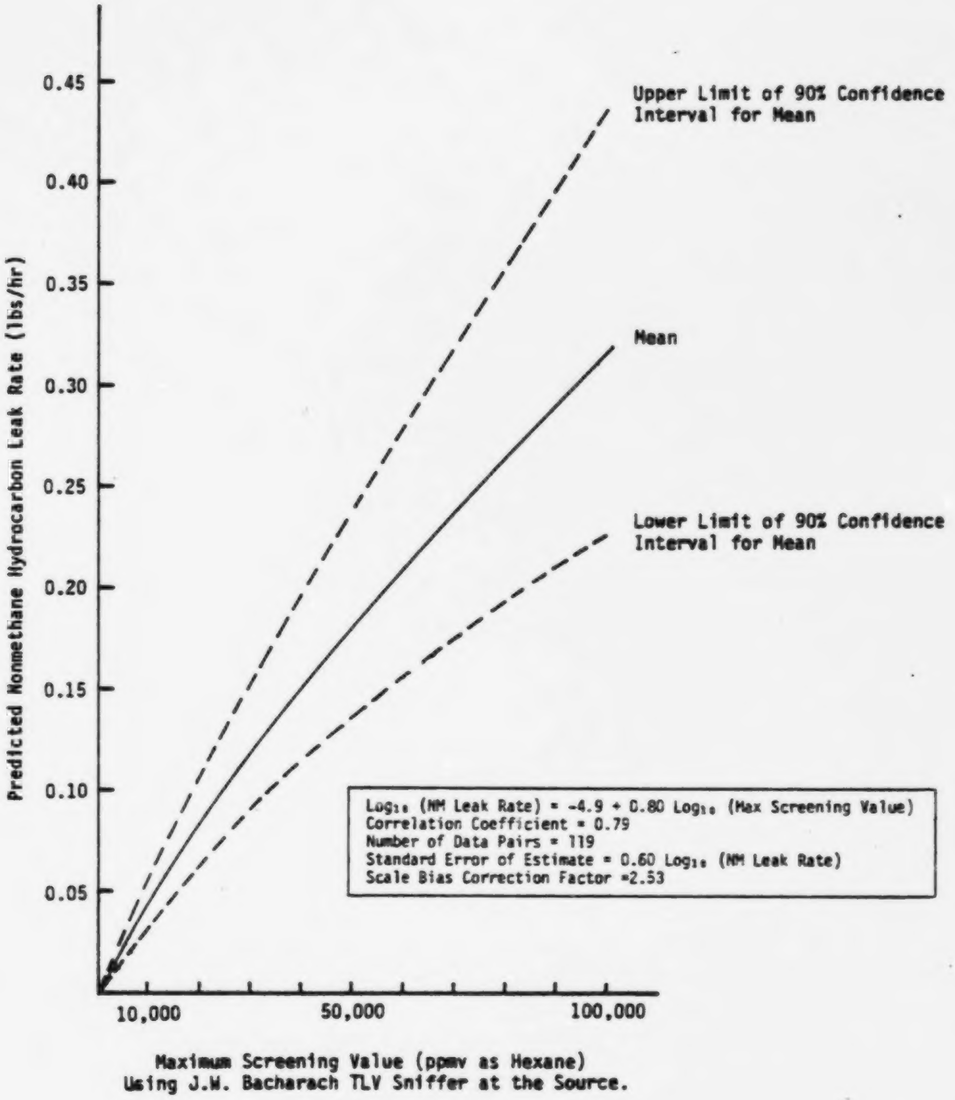


Figure 5-7B. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Light Liquid/Two-Phase Streams (Part II: Screening Values from 0 - 100,000 ppm).

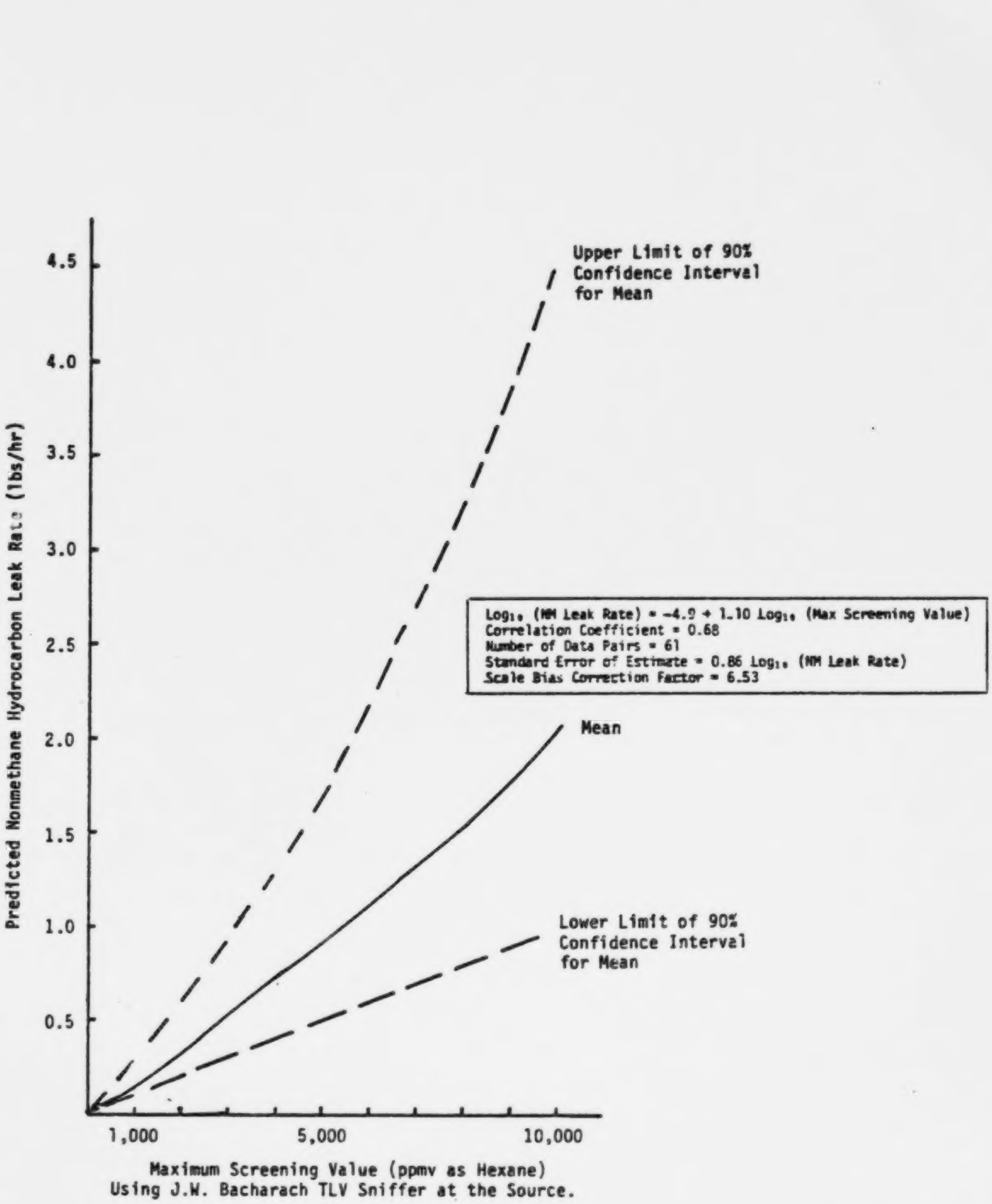


Figure 5-8. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Drains.

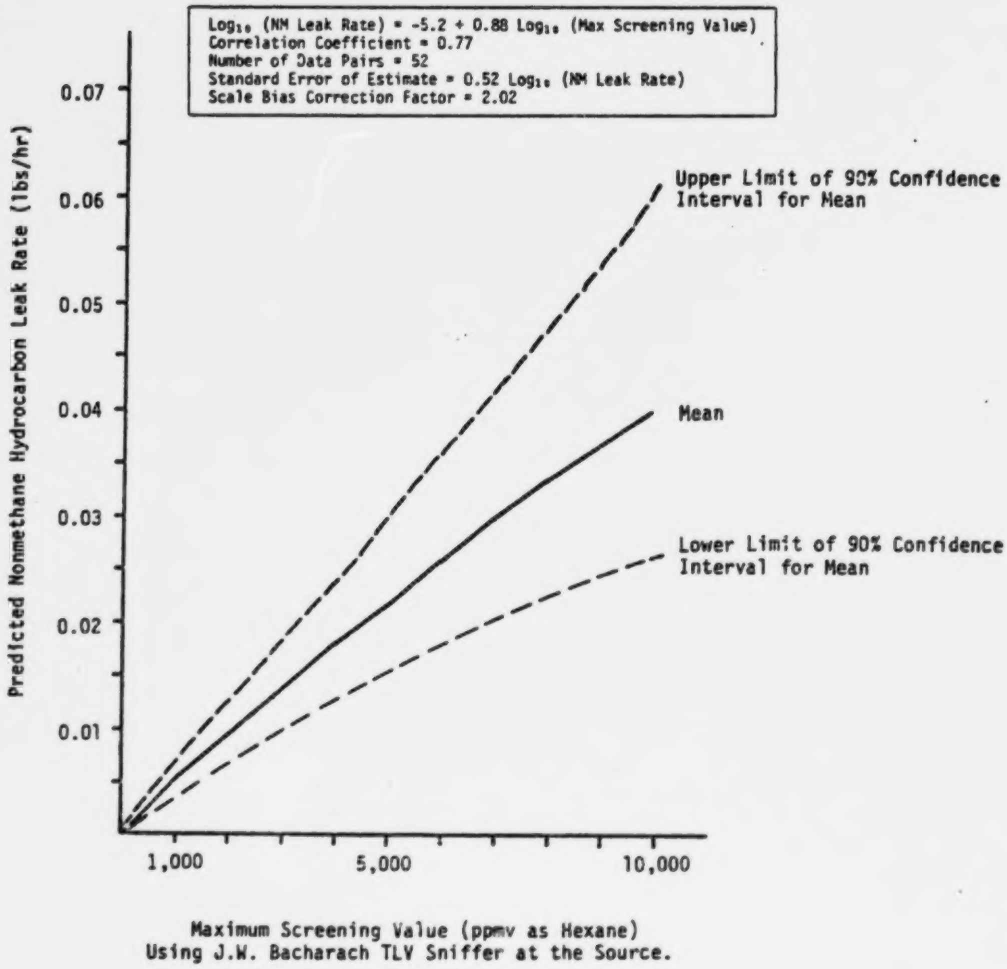


Figure 5-9. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Flanges.

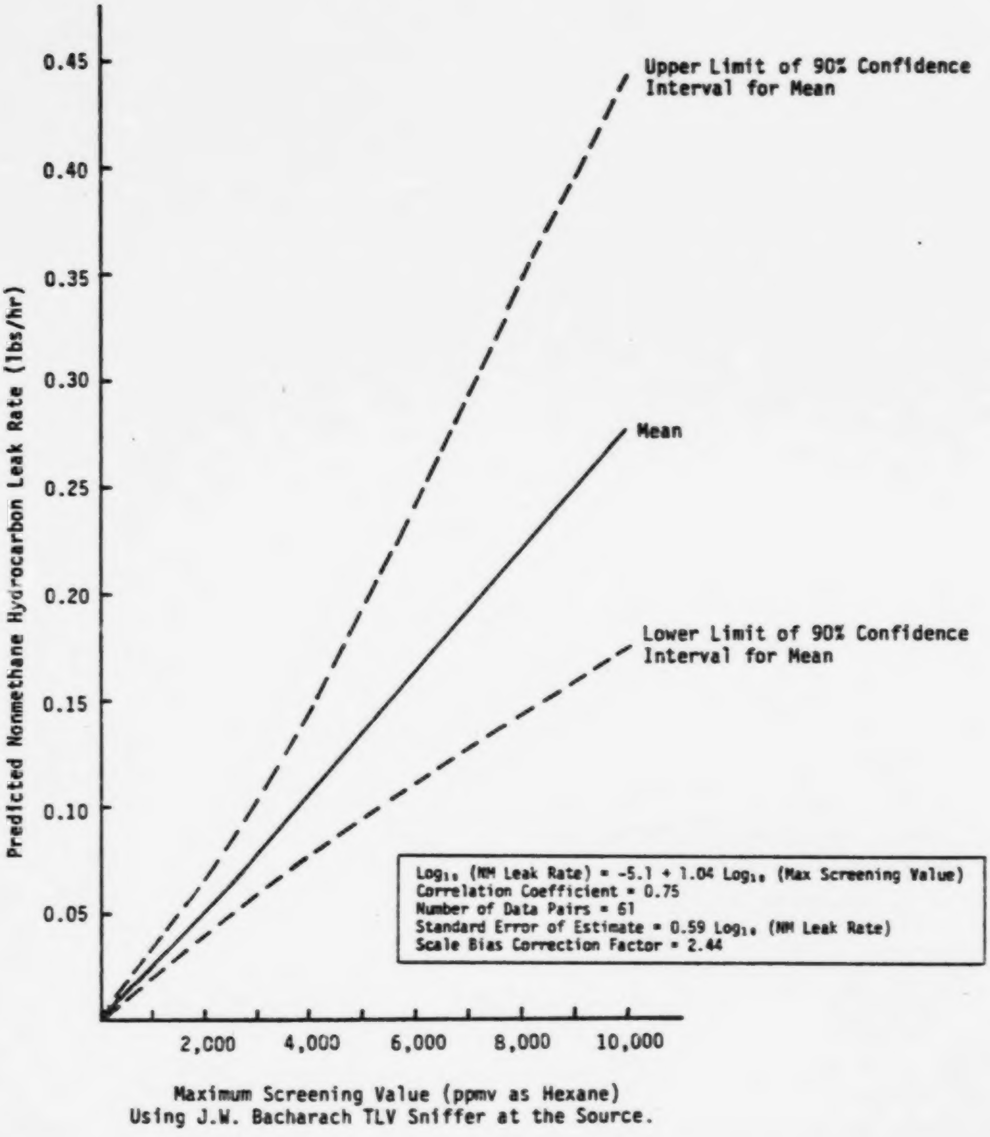


Figure 5-10A. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Pumps, Heavy Liquid Streams (Part I: Screening Values from 0 - 10,000 ppm).

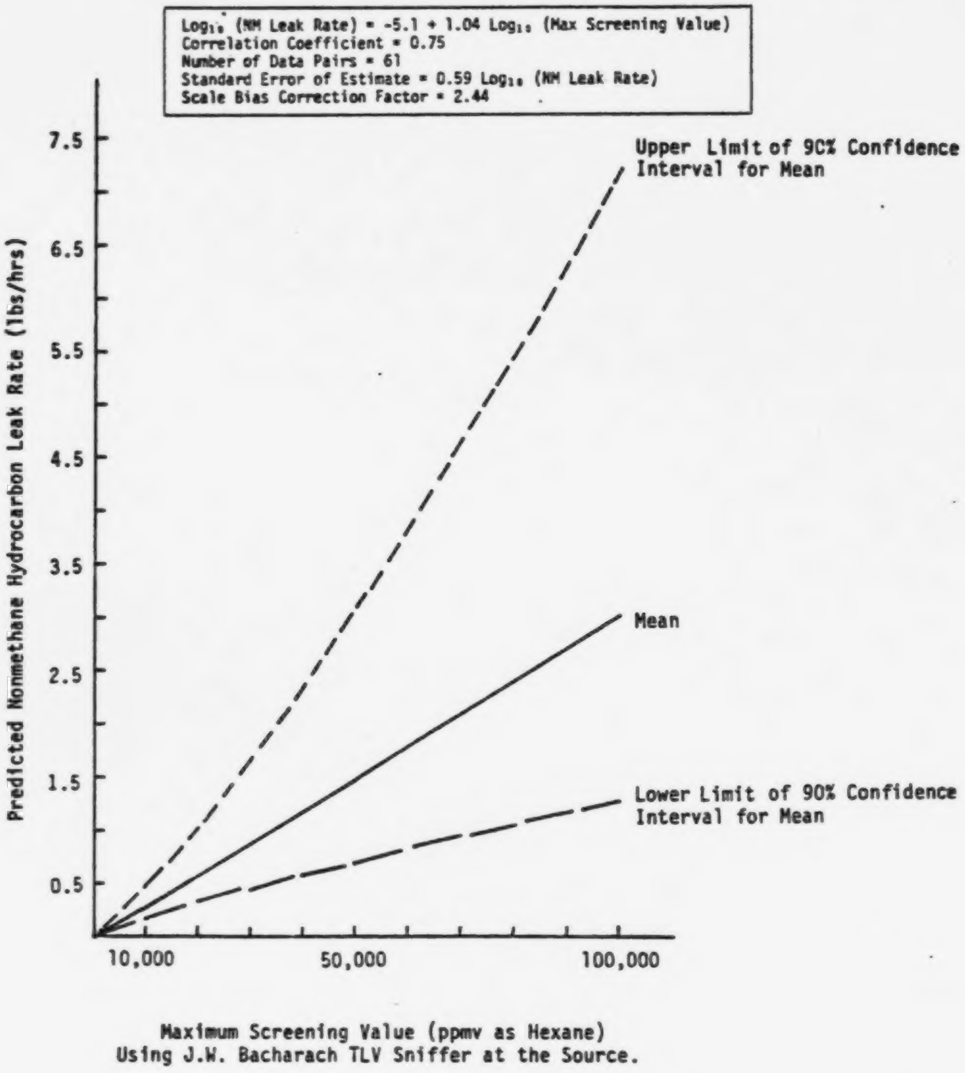


Figure 5-10B. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Pumps, Heavy Liquid Streams (Part II: Screening Values from 0 - 100,000 ppm).

TABLE 5-9. CONFIDENCE INTERVALS FOR MEAN AND INDIVIDUAL LEAK RATES - VALVES (GAS/VAPOR STREAMS)

Value (ppmv)	Predicted Mean Leak Rate (lb/hr)	90% Confidence Interval	
		Mean Leak (lb/hr)	Individual Leak (lb/hr)
1	4×10^{-7}	(10^{-7}, 3.6×10^{-6})	(0.0, 1.67×10^{-5})
200	0.00030	(0.00010, 0.00089)	(1.3×10^{-5}, 0.0071)
500	0.00094	(0.00038, 0.00023)	(4.3×10^{-5}, 0.021)
1 000	0.0022	(0.0010, 0.0048)	(0.00010, 0.047)
3,000	0.0085	(0.0048, 0.015)	(0.00042, 0.17)
5,000	0.016	(0.0097, 0.026)	(0.00080, 0.32)
10,000	0.038	(0.025, 0.057)	(0.0019, 0.75)
20,000	0.089	(0.063, 0.13)	(0.0045, 1.75)
50,000	0.27	(0.19, 0.39)	(0.014, 5.4)
100,000	0.64	(0.43, 0.96)	(0.032, 13.0)

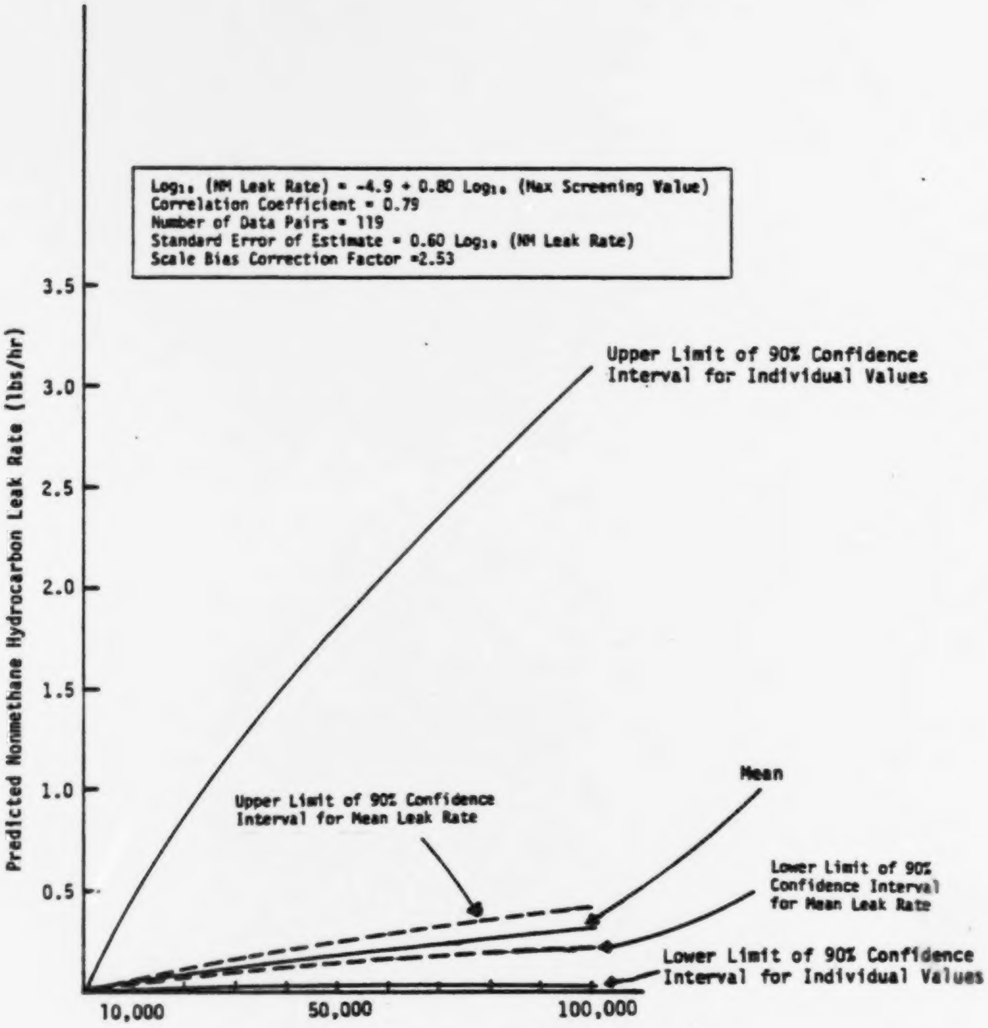


Figure 5-11. Nomograph for Predicting Total Nonmethane Hydrocarbon Leak Rates from Maximum Screening Values - Valves, Light Liquid/Two-Phase Streams (Part II: Screening Values from 0 - 100,000 ppm).

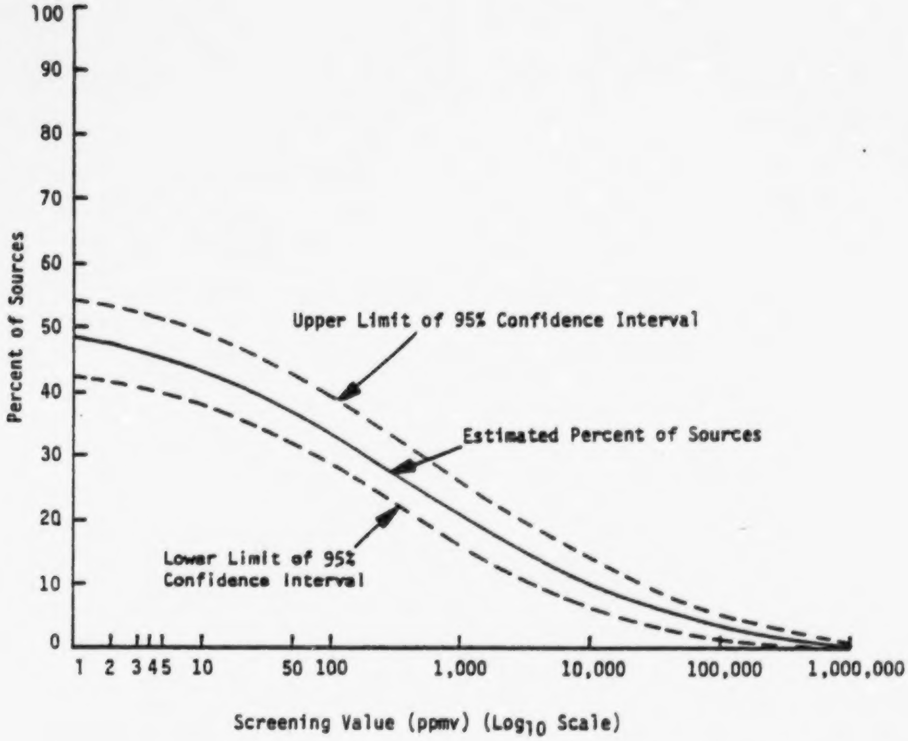
These nomographs for the six source types (and stream groups for valves, compressors, and pump seals) are presented in Figures 5-12 (A & B) through 5-22(A & B). The "A" figures relate the percent of total mass emissions for a given source category to screening values; the "B" figures relate the percent of sources to screening values.

Confidence intervals are included on each of these nomographs. The statistical procedures used to develop these intervals are discussed in Appendix C (Volume 4). The confidence intervals for both types of nomographs indicate how well the cumulative function has been estimated from the data collected in this program.

The 95 percent confidence intervals for the cumulative percent of sources can be interpreted as ranges of values which contain the actual percent from the population of sources studied.

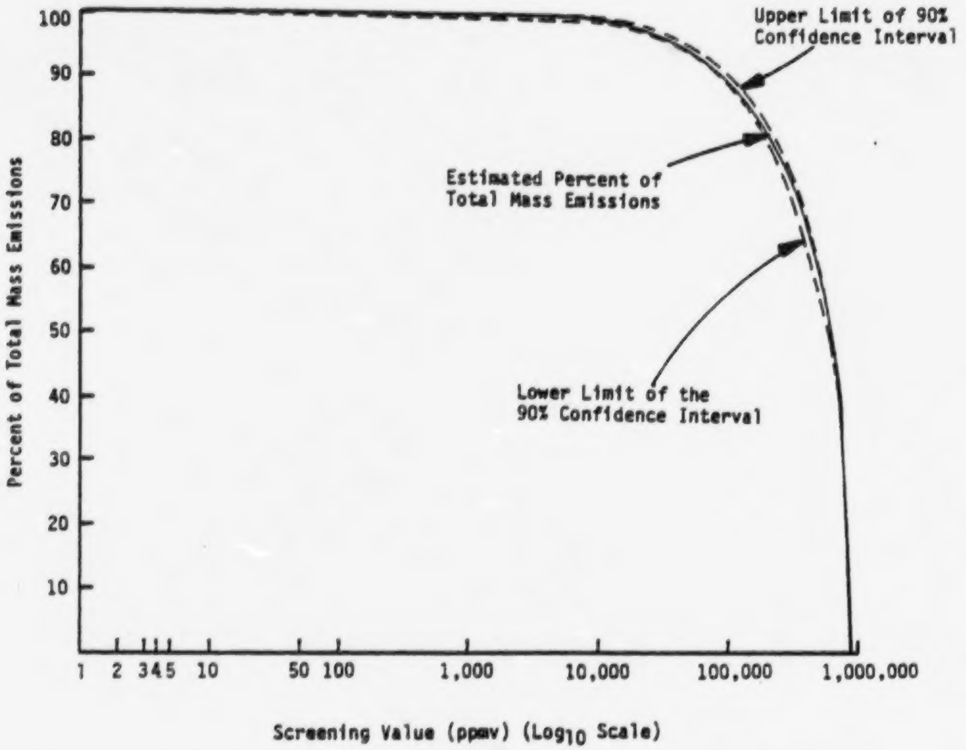
The 90 percent confidence interval for the cumulative percent of total emissions function has a similar interpretation. These intervals describe how well the function has been estimated for the entire population and are not directly applicable to a particular refinery situation with a finite number of sources. The variation of the function for a particular sample of sources is a complex function of the number of sources. Because of the nature of the function, however, the confidence intervals will be approximately valid any time a random sample of greater than 100 sources is being considered.

The nomographs are useful in evaluating the potential effectiveness of maintaining and repairing sources for reducing emissions. For example, approximately five percent of valves in gas vapor stream service can be expected to have screening values above 50,000 ppmv (Figure 5-12A). However, these five percent of the valves are responsible for an estimated 95 percent of the mass emissions (Figure 5-12B). Similarly, for a screening value of 10,000 ppmv, the percent of sources and percent of emissions are nine percent and 99 percent, respectively.



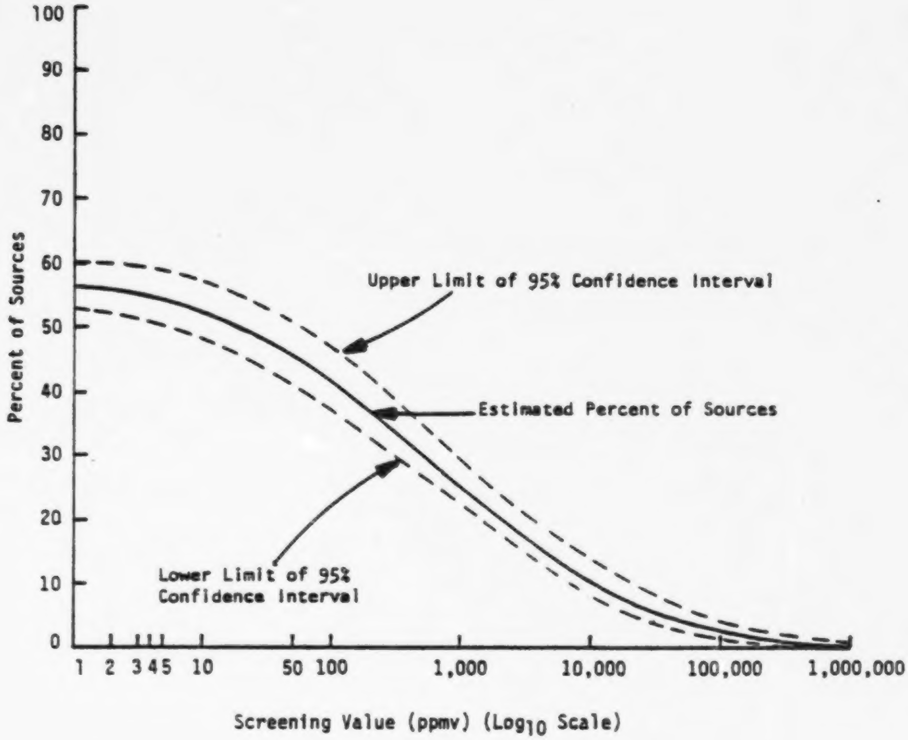
Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-12A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Valves - Gas/Vapor Streams.



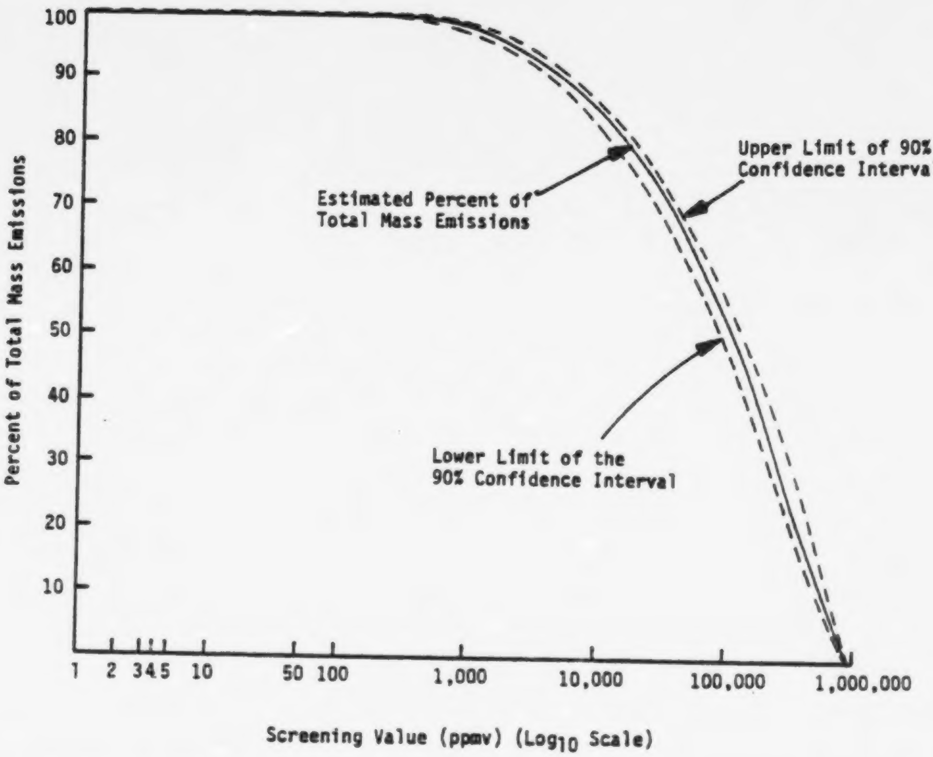
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-12B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Gas/Vapor Streams.



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-13A. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Light Liquid/Two-Phase Streams.



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-13B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Light Liquid/Two-Phase Streams.

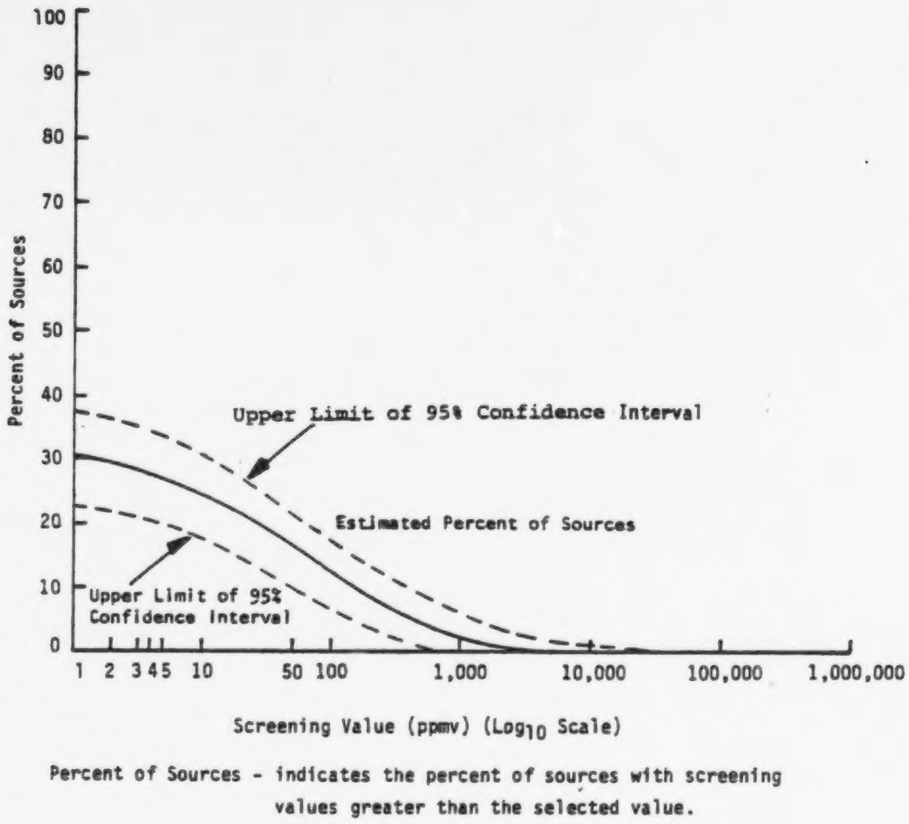
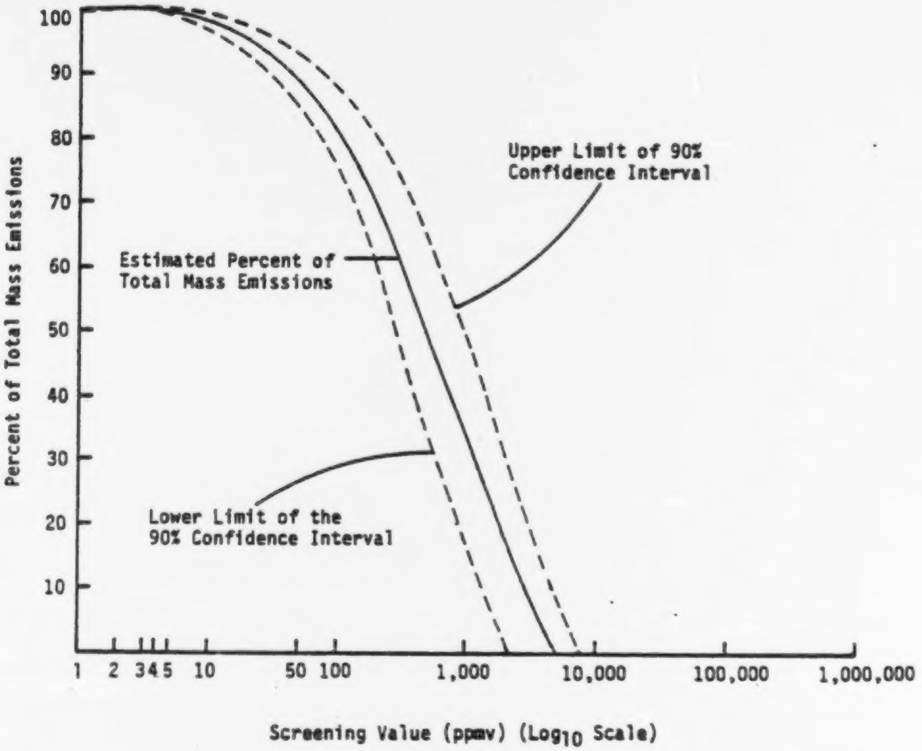
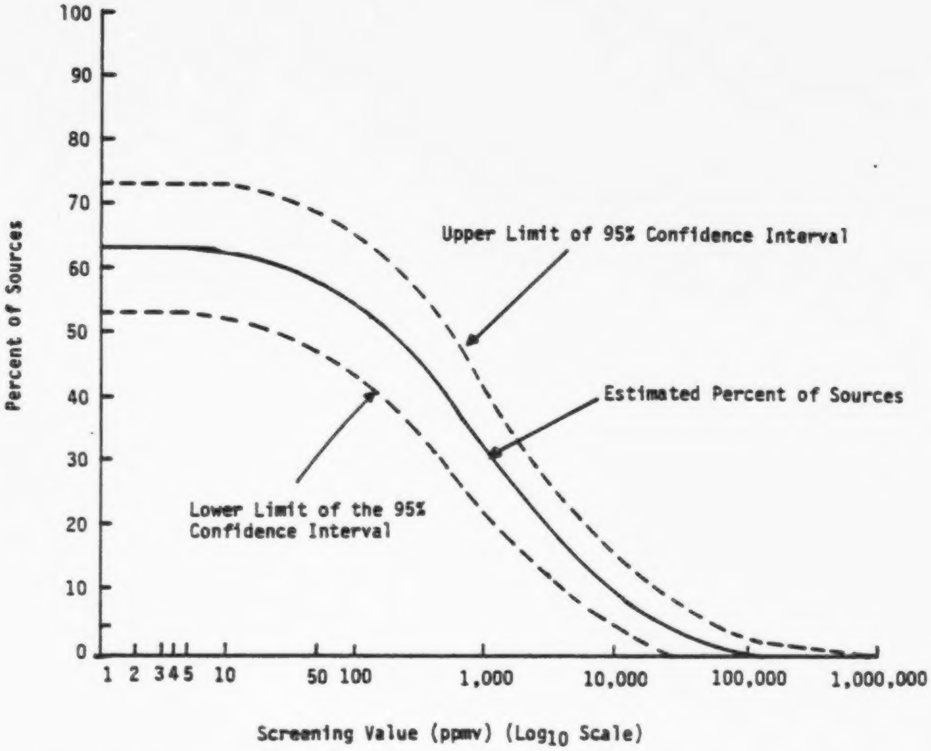


Figure 5-14A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Valves - Heavy Liquid Streams.



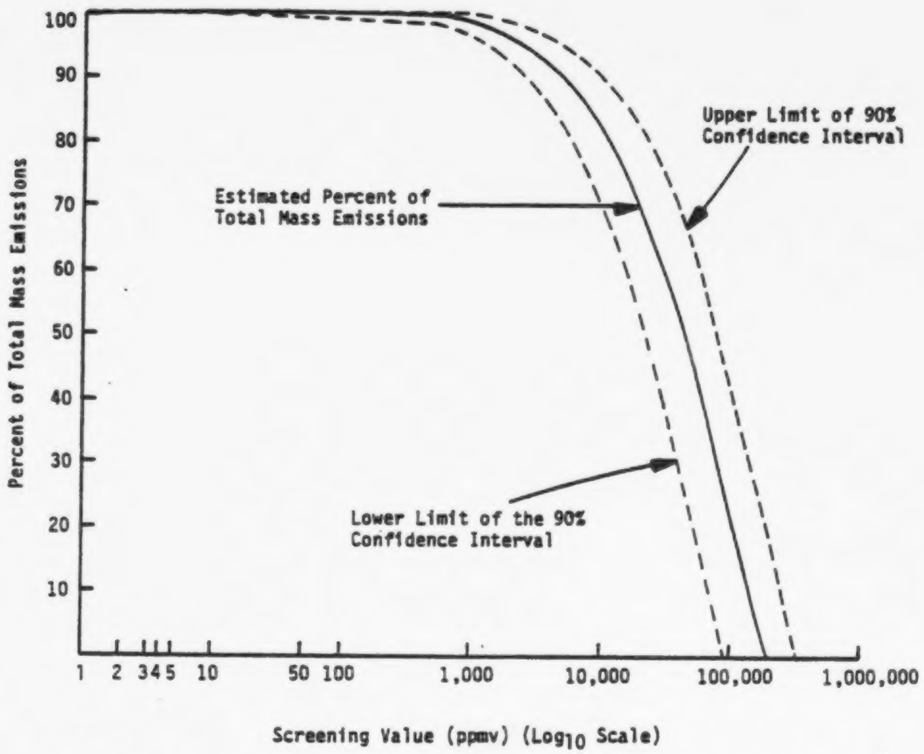
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-14B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Heavy Liquid Streams.



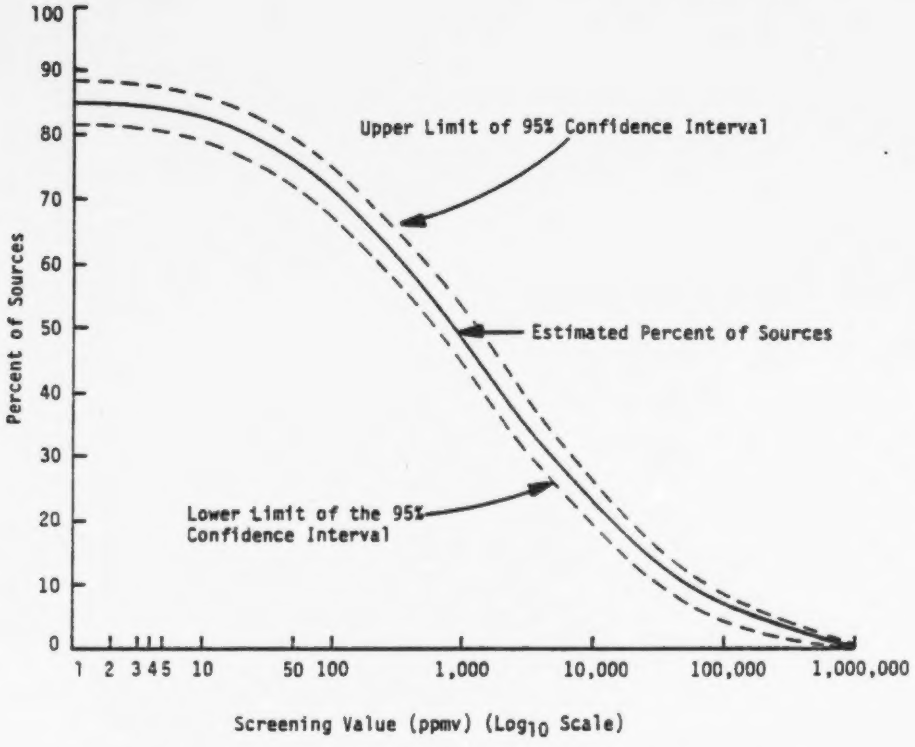
Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-15A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Valves - Hydrogen Service.



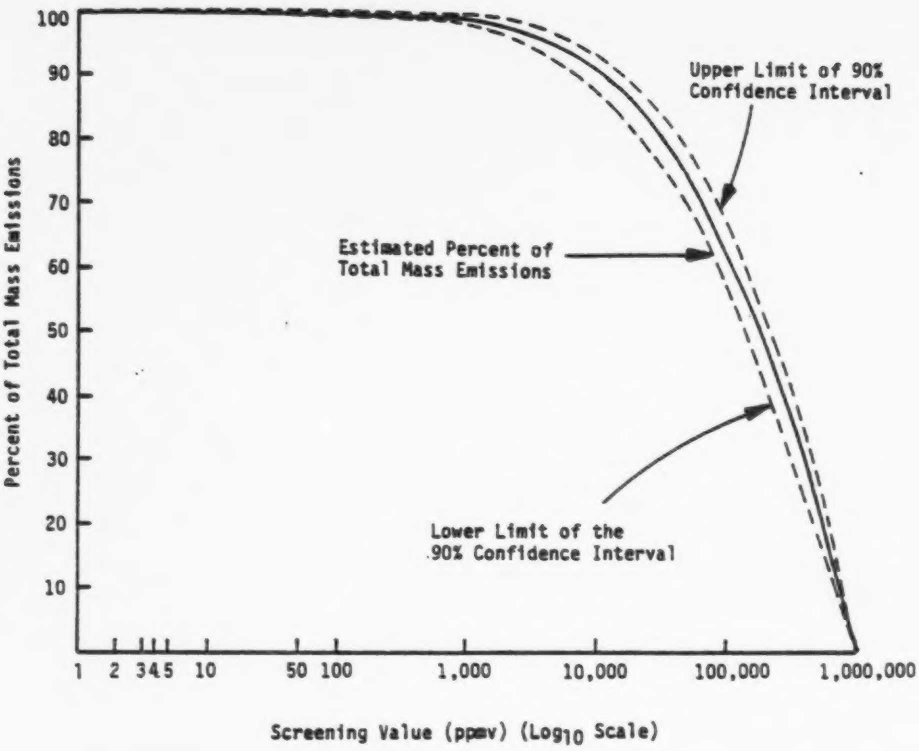
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-15B. Cumulative Distribution of Source and Total Emissions by Screening Values for Valves - Hydrogen Service.



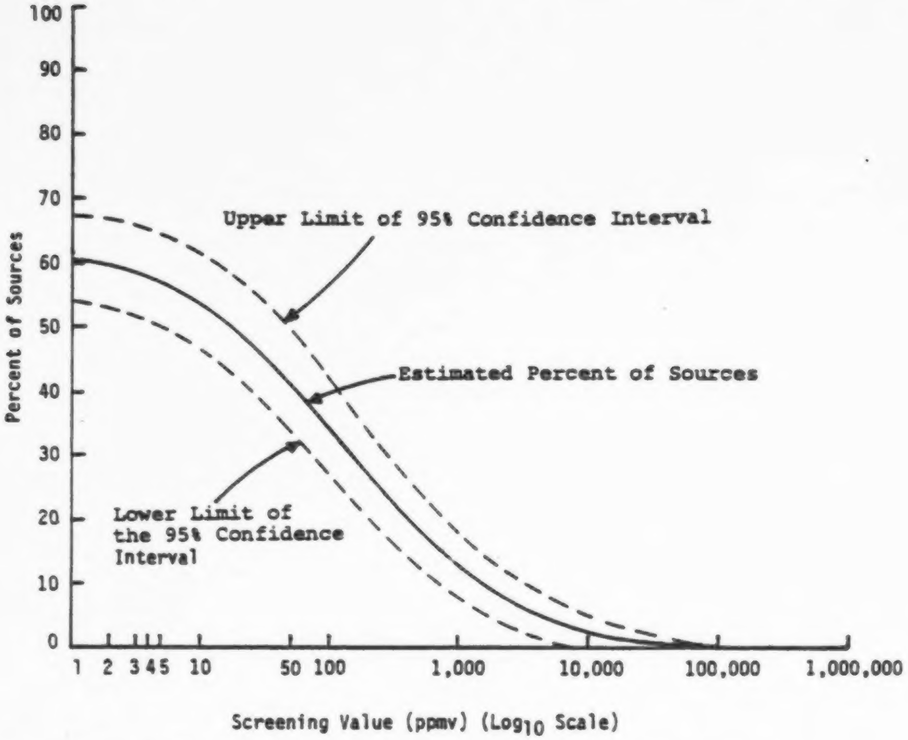
Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-16A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Pump Seals - Light Liquid Streams.



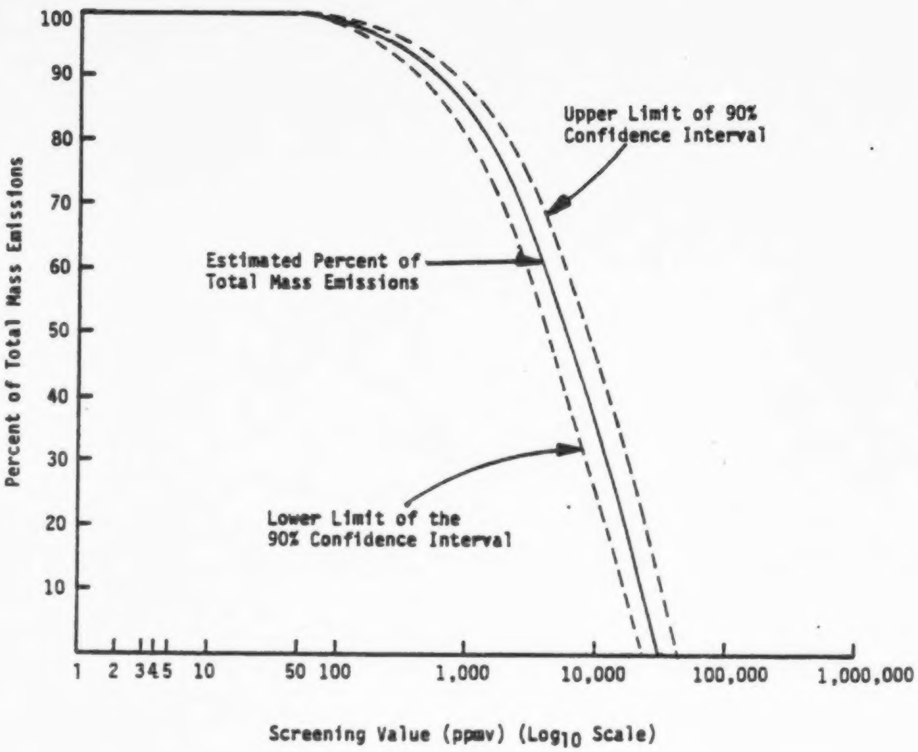
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-16B. Cumulative Distribution of Source and Total Emissions by Screening Values for Pump Seals - Light Liquid Streams.



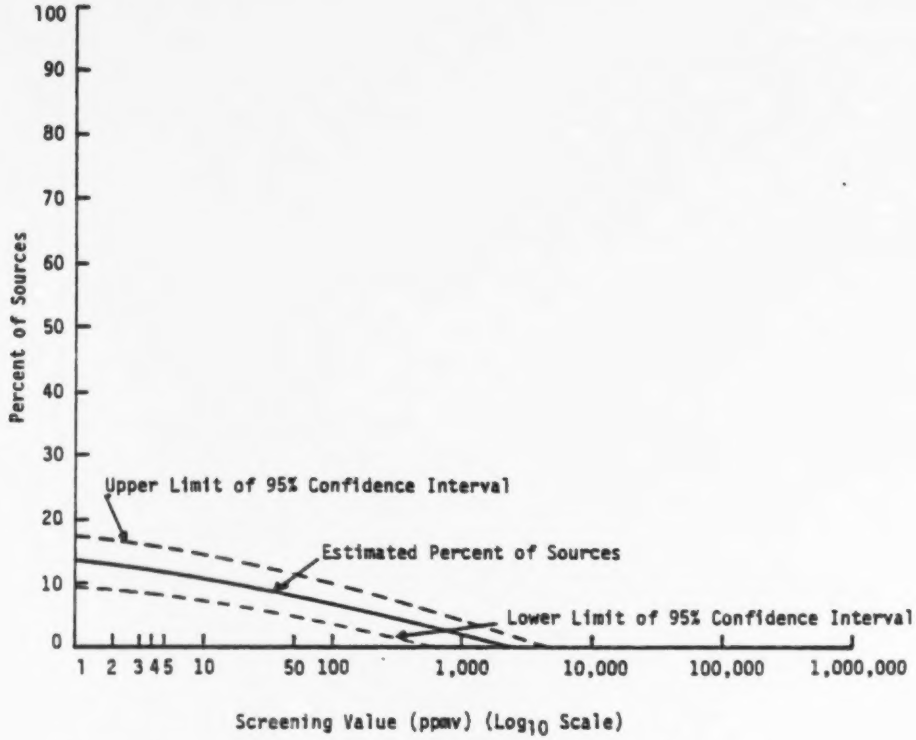
Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-17A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Pump Seals - Heavy Liquids.



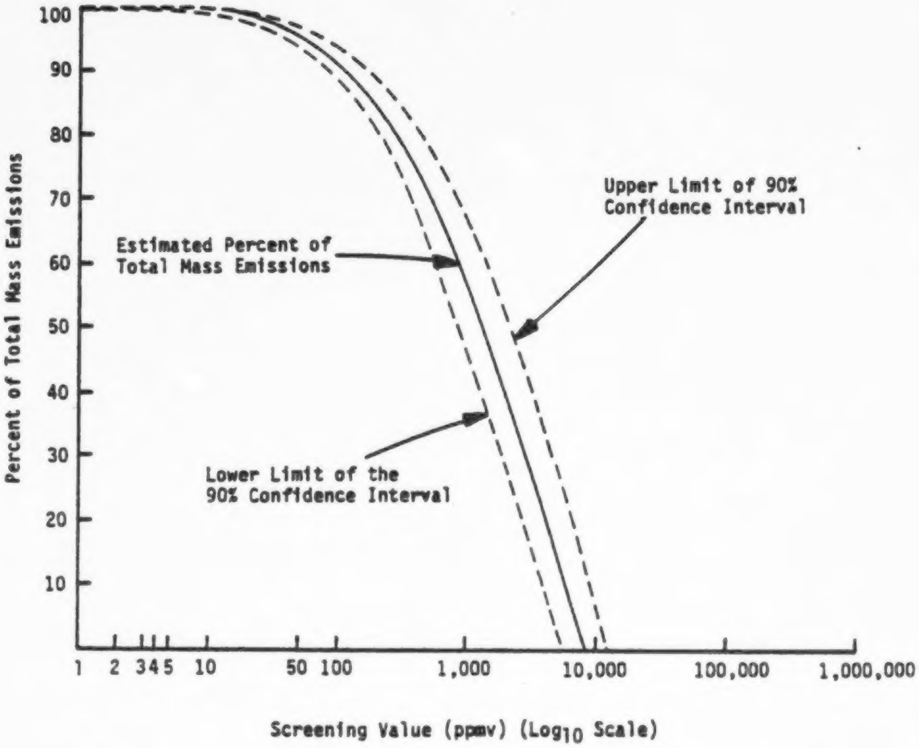
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-17B. Cumulative Distribution of Source and Total Emissions by Screening Values for Pump Seals - Heavy Liquids.



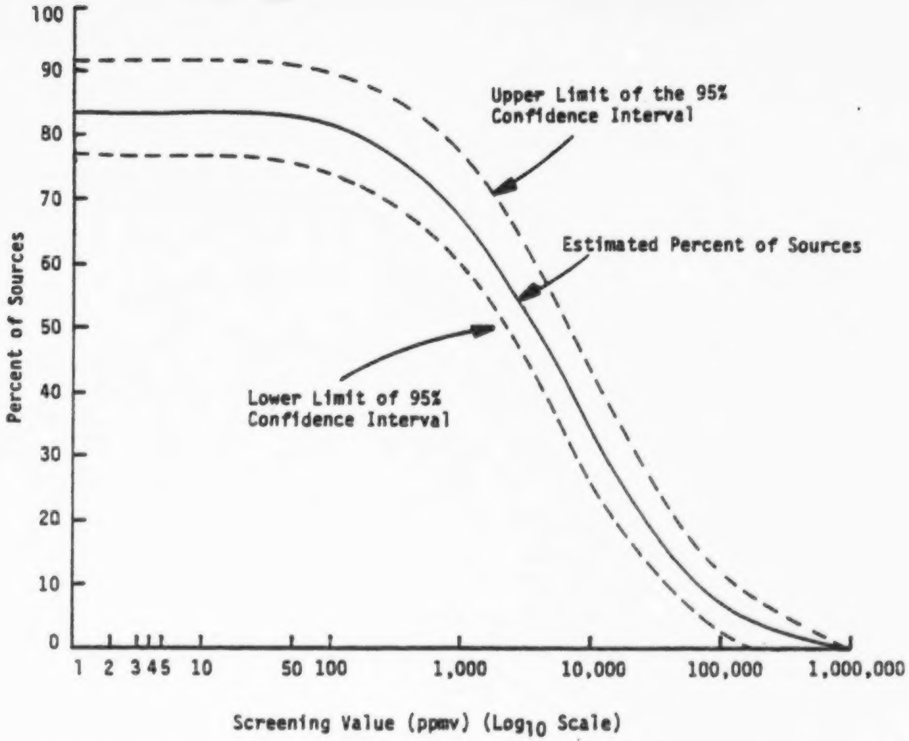
Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-18A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Flanges.



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-18B. Cumulative Distribution of Source and Total Emissions by Screening Values for Flanges.



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-19A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Compressor Seals - Hydrocarbon Service.

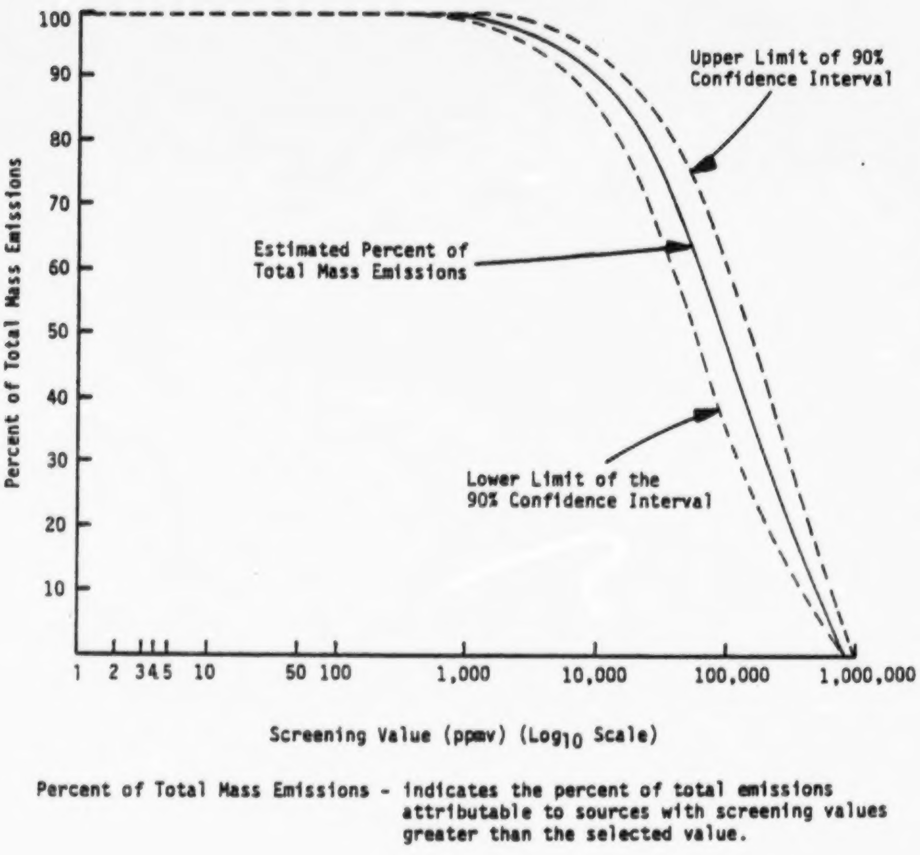
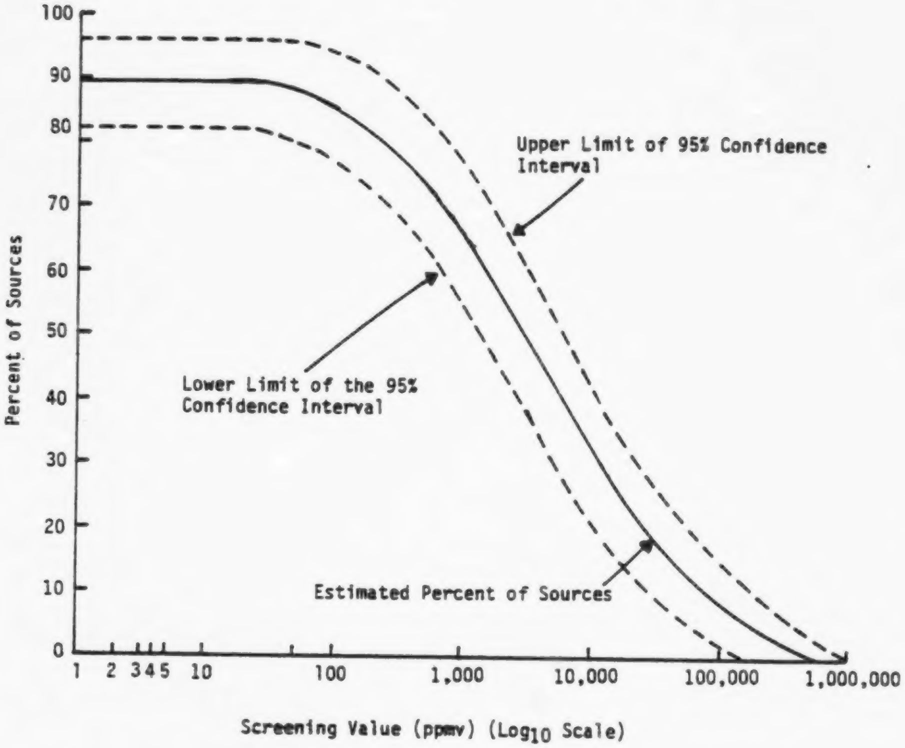
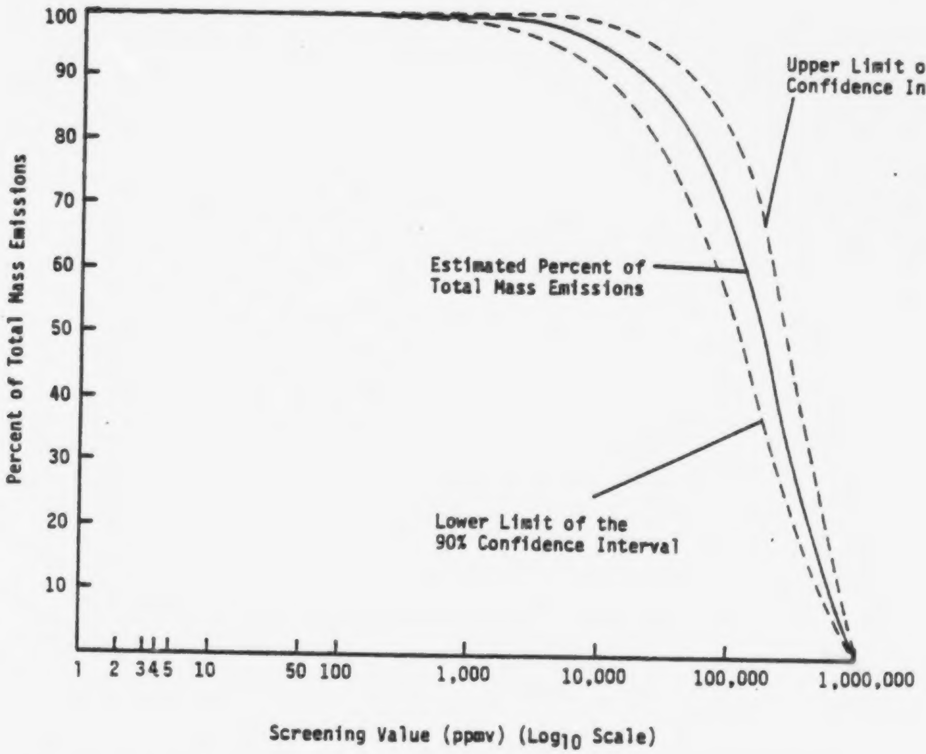


Figure 5-19B. Cumulative Distribution of Source and Total Emissions by Screening Values for Compressor Seals - Hydrocarbon Service.



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-20A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Compressor Seals - Hydrogen Service.



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-20B. Cumulative Distribution of Source and Total Emissions by Screening Values for Compressor Seals - Hydrogen Service.

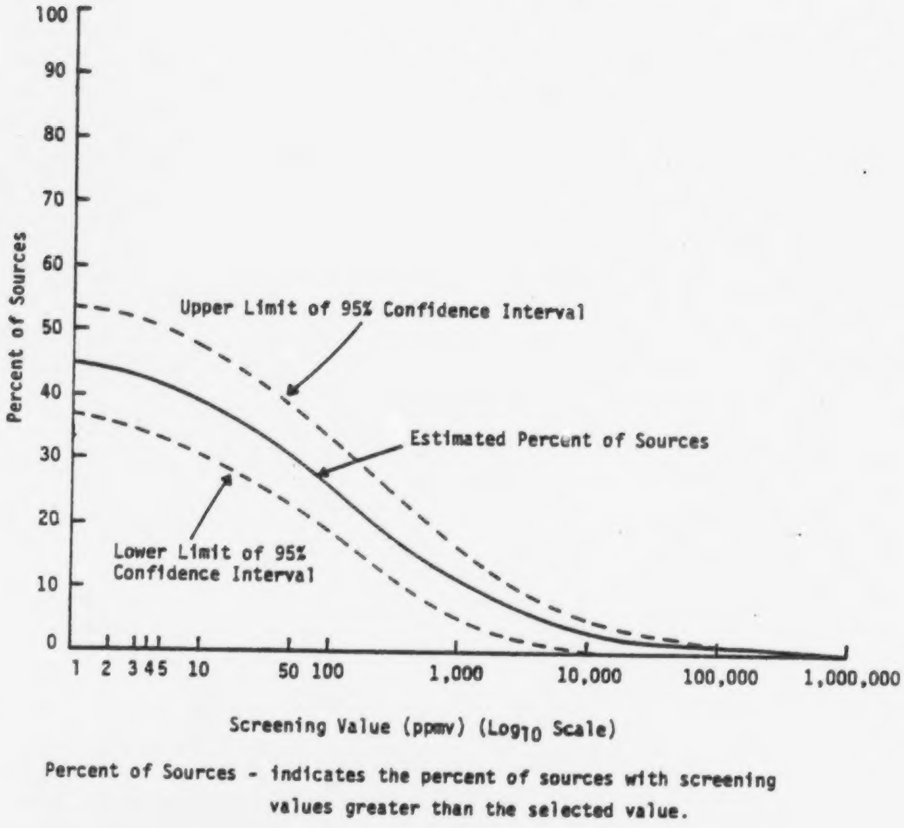
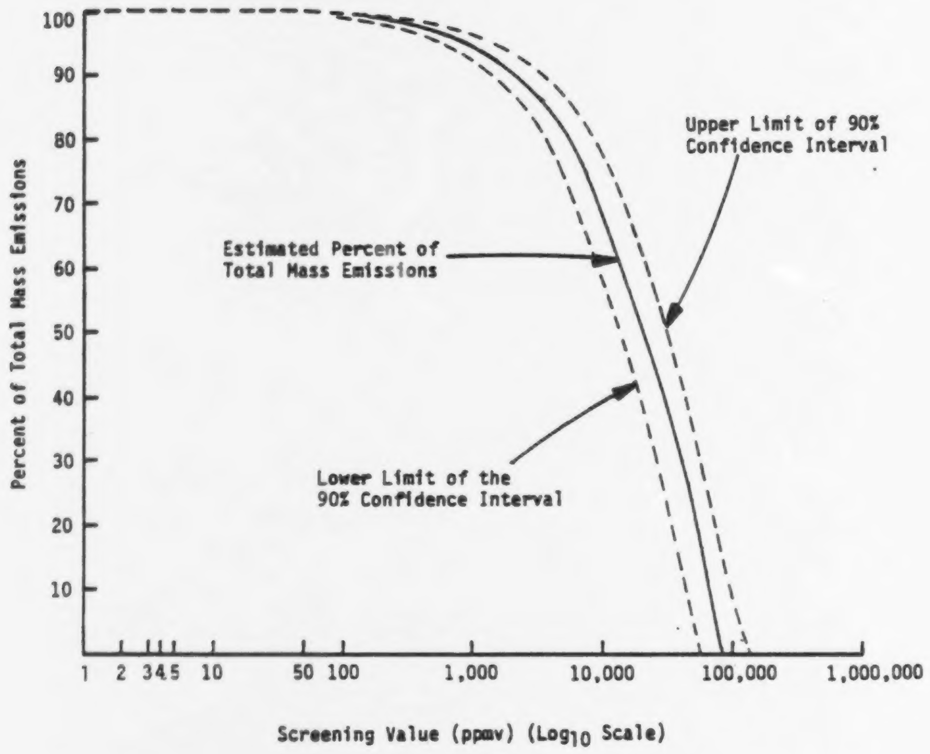
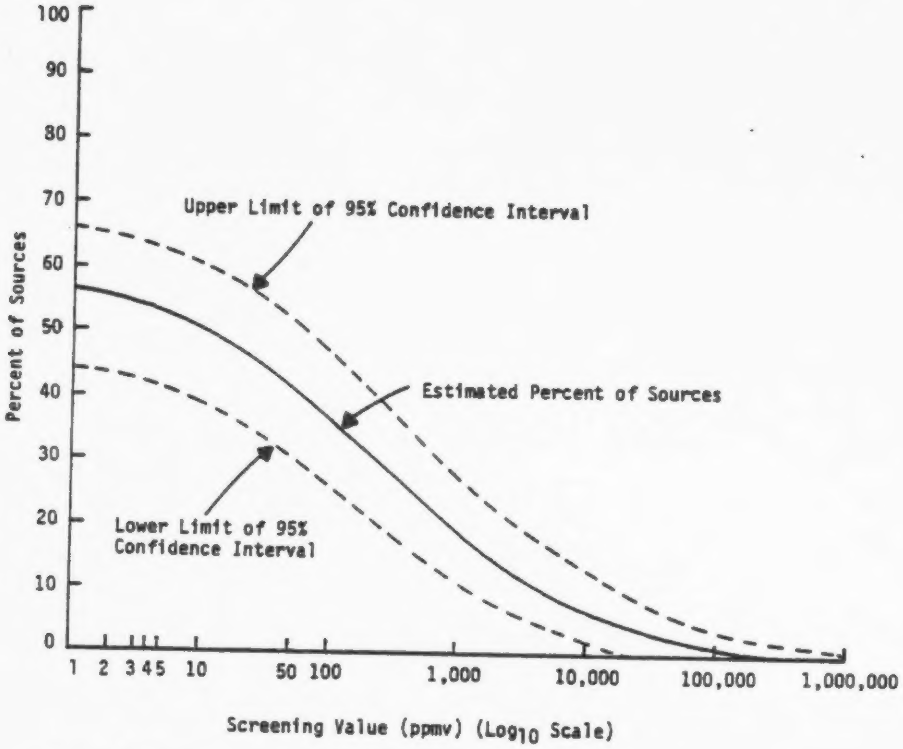


Figure 5-21A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Drains.



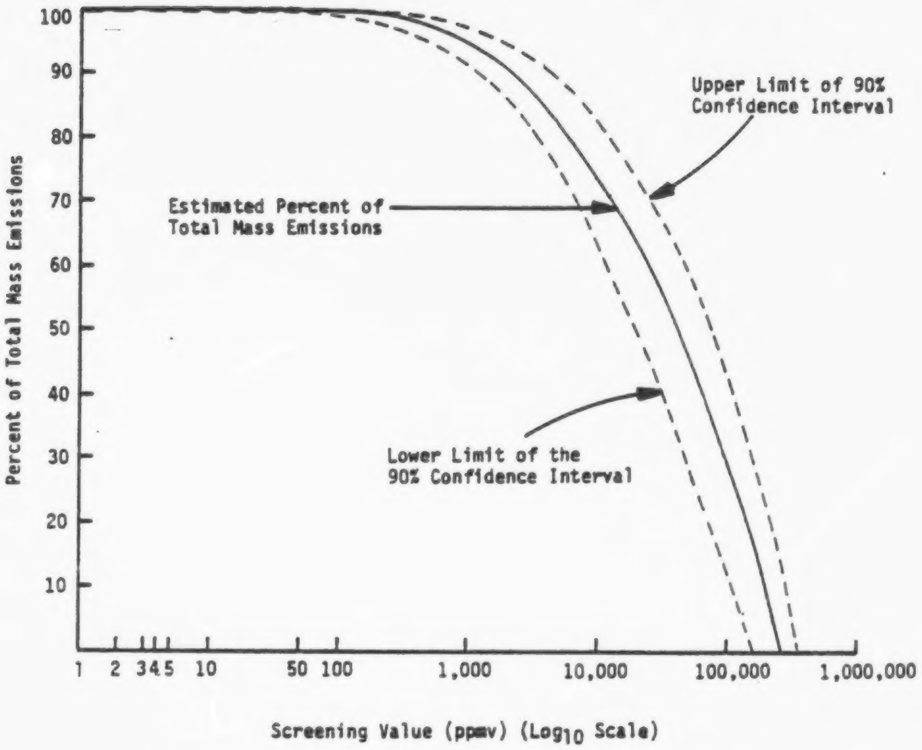
Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-21B. Cumulative Distribution of Source and Total Emissions by Screening Values for Drains.



Percent of Sources - indicates the percent of sources with screening values greater than the selected value.

Figure 5-22A. Cumulative Distribution of Sources and Total Emissions by Screening Values for Relief Valves.



Percent of Total Mass Emissions - indicates the percent of total emissions attributable to sources with screening values greater than the selected value.

Figure 5-22B. Cumulative Distribution of Source and Total Emissions by Screening Values for Relief Valves.

Analyses, using the nomographs, can also be done for other sources and process streams. For example, Table 5-10 shows the percent of emissions for various sources and process streams when the upper 10 percent of screened sources are considered. Confidence intervals are also shown. Table 5-10 is presented only to illustrate the use of the nomographs and to emphasize the fact that a small fraction of the sources within any one source category account for the majority of emissions in that category. There is no intent here to prejudge that a reasonable level of control is 10 percent of sources, or any other specific number. Ultimately, the decision regarding reasonable control will be based on relative levels of emission reduction and the cost of achieving these levels. Therefore, percentage reduction goals for each source category may be different.

5.1.4 Correlation of Leak Rates with Process and Equipment Variables

The relationships of various continuous process variables and other discrete variables with leak rates were investigated. The variables which were considered in this investigation are listed in Table 5-11. The results of the study are summarized in the discussion below. A more detailed discussion is given in Appendix B (Volume 3) of this report.

Correlation of Leak Rate with Continuous Variables--The correlation studies were complicated by three factors:

(a) The degree of skewness in the leak rate data and the inherent variability of the measured leak rates.

(b) The dominating effect of process stream composition on the leak rate.

(c) Inaccuracies or missing values when determining the values of variables.

TABLE 5-10. PERCENT OF TOTAL MASS EMISSIONS RELEASED BY THE UPPER[a] TEN PERCENT OF SCREENED SOURCES

	Minimum Screening Value (ppmv)	95% Confidence Interval for Percent of Sources	Percent of Total Emissions	
			Mean	90% Confidence Interval
Valves				
Gas/Vapor	9,200	(6, 13)	99	(98, 100)
Light Liquid/Two-Phase	11,000	(7, 13)	85	(82, 87)
Heavy Liquid	120	(5, 15)	80	(74, 87)
Hydrogen Service	9,400	(3, 16)	83	(70, 91)
Pump Seals				
Light Liquid	47,000	(7, 13)	75	(71, 79)
Heavy Liquid	1,100	(5, 15)	81	(76, 86)
Compressor Seals				
Hydrocarbon Service	68,000	(4, 15)	59	(46, 72)
Hydrogen Service	76,000	(3, 17)	77	(64, 87)
Flanges	14	(6, 14)	99	(98, 100)
Drains	1,100	(4, 16)	94	(92, 96)
Relief Valves	4,700	(3, 17)	83	(78, 90)

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[a] The upper ten percent of screened sources is defined as the ten percent of sources having the highest screening values.

TABLE 5-11. CONTINUOUS AND DISCRETE VARIABLES CONSIDERED IN THIS STUDY

Variable	Source Types Considered
Continuous:	
Temperature	All Source Types
Pressure	Valves, Flanges, Pump Seals, Compressor Seals, Relief Valves
Age	All Source Types
Size	All Source Types
Speed	Pump Seals, Compressor Seals
Capacity	Pump Seals, Compressor Seals
Load	Compressors
Stroke Length	Pump Seals, Compressor Seals
Discrete:	
Manufacturer	Valves, Flanges, Pump Seals, Compressor Seals, Relief Valves
Seal Type, Number	Pump Seals, Compressor Seals
Pump Type	Pump Seals
Valve Type	Valves
Valve Service	Valves
Stem Movement	Valves
Vibration	Valves, Flanges
Location on Line (In-line, End-of-line)	Valves
In/Out of Service	Valves, Pump Seals, Compressor Seals
Lubricant	Pump Seals, Compressor Seals
Attitude	Pump Seals
Materials of Construction	Valves, Flanges, Pump Seals, Compressor Seals, Relief Valves
Gland Type	Pump Seals, Compressor Seals

The logarithm (base 10) of the leak rate (lb/hr) was related to the variables to reduce the effect of skewness and variability of leak rate data. The data were grouped by the important process stream classifications to minimize the effect of the stream composition. Table 5-12 contains the simple correlation coefficients between the log leak rate and the appropriate independent variable for each source type and stream classification. The simple correlation coefficient, r, is a statistical measure of the linear relationship between two variables. Values of r fall between -1 and $+1$. Values of r near $+1$ mean that one variable increases proportionally to the other. Negative values of r indicate that one variable decreases as the other increases. The value of r will be zero if the data are randomly scattered.

The value of r^2 indicates the approximate percentage of the total variation in the log leak rate that is accounted for by the relationship of the leak rate with the correlating variable. For instance if $r = 0.50$, then $r^2 = 0.25$ and about 25 percent of the variation in the leak rate is attributable to the relationship with the process variable. The remaining 75 percent of the variation is due to other variables and random variation.

The statistically significant correlation coefficients are indicated with an asterisk in Table 5-12. A clearer indication of the significance of the correlations can be seen from a scatter plot of the data. Scatter plots for all correlations are given in Appendix B (Volume 3).

Relationships Between Discrete Variables and Leak Rates--Unlike continuous variables, correlation coefficients are not easily interpreted for discrete variables, i.e., manufacturer, material, and seal type versus leak rate. A visual method for comparing the relationships between levels of the discrete variables and leak rates is the schematic plot. Schematic plots show the mean, median, upper/lower quartile and range of leak rate values. Schematic plots are contained in Appendix B (Volume 3). The results can be briefly summarized.

TABLE 5-12. CORRELATIONS[b] BETWEEN CONTINUOUS VARIABLES AND LOG_{10} LEAK RATE

	Pressure	Temperature	Age	Line Size	Diameter	Area	RPM	Capacity	Load	Stroke Length
Valves										
Gas/Vapor Streams	.230*	.077	.263*	.150*	-	-	-	-	-	-
Light Liquid Streams	.103*	.051	.096	.143*	-	-	-	-	-	-
Heavy Liquid Streams	-.351*	.144	.220	.046	-	-	-	-	-	-
Hydrogen Service	-.088	.129	-.531*	.288*	-	-	-	-	-	-
Open-Ended	.236	.242	.230	-.078	-	-	-	-	-	-
Pump Seals										
Light Liquid Service	.088	-.012	.062	-	.021	-	-.064	-	-	-
Heavy Liquid Service	.097	-.098	.237	-	.128	-	-.182	-	-	-
Flanges	.072	.021	-.180	.336*	-	-	-	-	-	-
Compressor Seals										
Hydrocarbon Service	.346*	.218*	.105	-	.278*	-	-.143[a]	-.138	-.087	-.012
Hydrogen Service	.398*	.312*	.052	-	.343*	-	-.034	.218	-.099	-.074
Drains	-	-.408*	-	-	-.039	-.191	-	-	-	-
Relief Valves	.045	.096	-	-.075	-	-	-	-	-	-

* Correlation Coefficient statistically different from zero (P > .90).

[a] Log_{10} RPM was correlated with $\log_{10}$ leak rate.

[b] Values shown in table are correlation coefficients, r. The correlation between X and Y is computed as

$$r_{XY} = \frac{\Sigma(X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\Sigma(X_i - \bar{X})^2 \, \Sigma(Y_i - \bar{Y})^2}}$$

and is bounded

$$-1 < r_{XY} < 1$$

When sample size is taken into consideration, there appears to be no significant correlation of valve leak rates with any of the discrete variables. For pumps in heavy liquid service, a small difference can be seen between single and double seals. However, the small sample size prevents any firm conclusions from being drawn regarding this difference.

Effect of Process Variables on Percent of Sources Leaking--Previous analyses have shown that the percent of leaking sources varies with the source type and process stream volatility. The effect of other process variables on the percent of leaking sources was examined. The results of this examination are presented in detail in Appendix B (Volume 3).

Some significant differences in percent leaking were noted for valves due to age and unit type and vibration. Valves less than one year old have a higher percent leaking for gas/vapor and light liquid streams, but not for heavy streams. The percentage of leaking valves increases with increasing line size. No significant differences were noted for the different valve manufacturers.

For pump seals in light liquid service, the percent of seals leaking appeared to increase as the pressure and temperature increased. No significant differences were noted for the discrete variables, including manufacturer. Single seals had a higher percent leaking than double seals for both light and heavy liquid streams, although the confidence intervals did overlap.

For compressors in hydrocarbon service, significant differences in the percent of seals leaking were noted for gland type and seal type. The percent leaking also appeared to be increasing as discharge pressure increased.

5.1.5 Effect of Maintenance Procedures on Valve Emissions

A study to define the short term effect of maintenance on valve emissions was conducted. The study was performed on 86 valves at four refineries. Routine maintenance, such as tightening the packing gland or adding grease, was performed on the selected valves. Maintenance is described as "directed" or "undirected." Directed maintenance involved simultaneous maintenance and screening of the valve until no further reduction in hydrocarbon detector reading could be achieved. Undirected maintenance was not monitored with a hydrocarbon detector during the performance of maintenance.

The screening value and emission rate for each valve was determined before and after maintenance. The percentage reduction in leak rates after maintenance was calculated with the following equation:

$$\text{\% Reduction} = \frac{\text{Leak Rate Before Maintenance} - \text{Leak Rate After Maintenance}}{\text{Leak Rate Before Maintenance}}$$

The effects of the valve maintenance studies are summarized in Table 5-13. Two results are noteworthy. The percentage leak reduction for those valves that were subjected to directed maintenance is considerably greater than that of the valves that had undirected maintenance. It is also apparent that the level of the initial leak rate has a marked effect on the percentage reduction in emission rate for both directed and undirected maintenance. The percentage reduction achieved by maintenance is lower for the initially small leak rates. In the very low initial leak range, ≤ 0.001 pounds per hour, the average and weight percent reduction was actually negative for undirected maintenance.

A statistical summary of the maintenance results is presented in Table 5-14. For directed maintenance, the median percent reduction is approximately constant across the screening value range. However, for the undirected maintenance group the median percent reduction increases

TABLE 5-13. SUMMARY OF MAINTENANCE REDUCTION BY LEAK RATE LEVEL

Level	Original Leak Rate Range (lb/hr)		Directed Maintenance	Undirected Maintenance
1	≤0.001	n	4	6
		$\overline{p}$	30.7	-105.5
		pw	35.2	-26.3
		pm	52.6	5.6
2	0.001 - 0.01	n	12	16
		$\overline{p}$	48.7	-530.0
		pw	56.9	-276.4
		pm	86.2	30.4
3	0.01 - 0.1	n	10	22
		$\overline{p}$	93.8	31.7
		pw	93.0	45.1
		pm	93.8	60.9
4	>0.1	n	1	15
		$\overline{p}$	98.0	73.4
		pw	98.0	83.5
		pm	98.0	85.4

n = Number of valves maintained

$$\overline{p} = \text{Average percent reduction} = \Sigma P_i/n, \text{ where } P_i = \frac{\text{(leakage before - leakage after maintenance)}}{\text{leakage before maintenance}} \times 100$$

$$pw = \text{Weight percent reduction} = \frac{\Sigma\text{leakage before maintenance} - \Sigma\text{leakage after maintenance}}{\Sigma\text{leakage before maintenance}} \times 100$$

pm = Median percent reduction

TABLE 5-14. STATISTICAL SUMMARY OF MAINTENANCE DATA - PERCENT REDUCTION

Screening Value Range (ppmv)	Directed Maintenance								
	Block Valves				Control Valves				
	G/V Stream	LL Stream	HL Stream	Total* Block	G/V Stream	LL Stream	HL Stream	Total Control	Total* All Valves
<5K	2 58.8 56.5 58.8	5 63.1 90.5 93.1	0	7 61.8 86.5 87.3	0	4 39.5 84.9 89.8	0	4 39.5 84.9 89.8	11 53.74 (3.7,100) 85.6 (72,99) 88.4 (18,98)
5K-50K	2 76.1 90.7 76.1	4 89.8 89.0 90.1	0	6 85.2 89.1 88.7	1 45.7 45.7 45.7	1 95.0 95.0 95.0	0	2 70.4 91.5 70.4	8 81.5 (65,98) 89.2 (69,100) 88.7 (-55,96)
>50K	3 93.8 97.8 98.0	2 -26.4 56.7 -26.4	0	5 45.7 92.3 91.7	1 77.2 77.2 77.2	2 97.2 96.4 97.2	0	3 90.5 95.0 94.5	8 62.5 (-7.9,100) 92.6 (81,100) 93.1 (-33,99)
				18 64.2 (32,96) 91.0 (82,99) 86.2 (75,97)				9 66.8 (12,100) 89.7 (79,99) 91.2 (9.3,98)	27 64.6 (38,91) 90.7 (83,98) 91.2 (79,95)

(Continued)

*Numbers in parentheses indicate an approximate 95% confidence interval for the average reduction for the three different estimations.

Code for Each Cell in Table

1	2
	3
	4

1 = Number of valves maintained

2 = Average of percent reduction where percent reduction = $\frac{\text{100 x (leak before - leak after maintenance)}}{\text{Leak before maintenance}}$

3 = Weight percent reduction = $\frac{\Sigma\text{leak rate before maintenance} - \Sigma\text{leak rate after maintenance}}{\Sigma\text{leak rate before maintenance}}$

4 = Median percent reduction

TABLE 5-14. Continued

	Undirected Maintenance								
	Block Valves				Control Valves				
Screening Value Range (ppmv)	G/V Stream	LL Stream	HL Stream	Total* Block	G/V Stream	LL Stream	HL Stream	Total Control	Total* All Valves
<5K	6 54.0 52.2 65.2	6 42.6 58.9 76.9	4 -26.1 -43.4 7.37	16 29.7 48.5 33.1	7 -1320 - 717 -58.4	5 5.2 91.1 26.56	0	12 - 769 -50.5 24.1	28 -312 (-950,100) 33.0 (-39,100) 28.9 (-0.5,79)
5K-50K	4 69.8 47.8 82.6	4 -64.9 - 9.0 28.2	0	8 2.4 20.2 50.1	2 54.2 53.8 54.2	4 87.8 96.9 95.6	1 82.1 82.1 82.1	7 77.4 90.2 82.1	15 37.4 (-28,100) 67.4 (34,100) 82.1 (42,88)
>50K	3 75.3 88.4 84.3	4 81.3 93.0 90.9	0	7 78.7 91.1 85.4	8 29.4 81.3 19.3	1 90.6 90.6 90.6	0	9 36.2 87.0 29.5	16 54.8 (31,78) 89.6 (81,98) 67.0 (21,92)
				31 33.7 (-1.8,69) 68.7 (48,89) 61.1 (31,85)				28 298 (-940,100) 81.0 (64,98) 51.4 (13,85)	59 -124 (-410,100) 73.9 (69,88) 53.8 (29,82)

*Numbers in parentheses indicate an approximate 95% confidence interval for the average percent reduction for the three different estimations.

Code for Each Cell in Table

1	2
	3
	4

1 = Number of valves maintained

2 = Average of percent reduction where percent reduction = $\frac{100 \times (\text{leak before} - \text{leak after maintenance})}{\text{Leak before maintenance}}$

3 = Weight percent reduction = $\frac{\Sigma\text{leak rate before maintenance} - \Sigma\text{leak rate after maintenance}}{\Sigma\text{leak rate before maintenance}} \times 100$

4 = Median percent reduction

dramatically with increasing screening values. Within the low screening value range the median percent reduction is very low, only 28.9 percent. This may indicate that undirected maintenance at this screening level is not effective at all.

5.1.6 Number and Distribution of Baggable Sources

The analyses of the emission rate data showed that the emission rates of hydrocarbons from valves, pump seals, and compressor seals were functions of the process stream properties. To estimate total hydrocarbon emissions from these sources in a complete refinery or in individual process units within refineries, the distribution and number of the sources in the various types of process stream services must be available.

As part of the refinery assessment program, individual fugitive emission sources were physically counted in a number of process units within five different refineries. Valves, flanges, pumps, compressors, drains, and relief valves (only those venting directly to the atmosphere) were counted. The counted sources are listed in Table 5-15. The capacities of each unit in which sources were counted are also presented.

Some sources are not included in this tabulation. Only those valves in hydrocarbon service on process, vent, or fuel lines were counted. Valves in auxiliary services such as steam, air, compressor lubrication, pump seal flushing, and sight glass shut-off were not included in the source numbers listed in Table 5-15.

Pumps and compressors operating on non-hydrocarbon streams such as water and air were not counted. Only those relief valves that were venting directly to the atmosphere were included as emission sources. Those relief valves venting into blowdown and flare systems were not included in the numbers given in Table 5-15. All drains in a unit were counted.

TABLE 5-15. SUMMARY OF HYDROCARBON EMISSION SOURCES COUNTED IN SELECTED REFINERY PROCESS UNITS

Process Unit	Unit Capacity BPSD	Valves	Flanges	Pumps	Compressors	Relief Valves[1]	Drains
Atmospheric Distillation: Unit A	50,000	1032	3720	33	0	0	102
Unit B	10,000	754	4274	28	1	4	36
Fuel Gas/Light Gas Processing: Unit A	--	152	658	0	4	30	7
Unit B	--	210	630	5	0	3	14
Catalytic Hydroprocessing: Unit A	16,000	632	3410	11	2	16	24
Unit B	10,000	658	2076	8	3	0	--
Fluid Catalytic Cracking: Unit A	9,000	1314	4212	30	4	16	65
Hydrocracking: Unit A	14,000	931	--	22	3	4	58
Catalytic Reforming: Unit A	11,000	660	2279	18	4	0	70
Unit B	5,000	943	3334	16	3	-	54
Unit C	3,000	470	3270	8	3	0	23
Alkylation: Unit A	6,000	571	1992	11	0	1	28
Unit B	2,000	782	2821	14	0	15	54
Fluid Coking: Unit A	7,000	304	1047	9	4	6	28
Dewaxing/Treating: Unit A	≈4,000	380	1950	16	0	4	43
Unit B	≈4,000	855	3435	19	4	0	43
Unit C	≈4,000	700	--	25	0	-	45
Unit D	--	459	1481	11	0	0	--
Hydrogen Plant: Unit A	20 MMCFD	182	635	5	-	4	17

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[1] Relief valves venting to the atmosphere.

All the sources were counted only within the battery limits of each process unit.

The visual source counts were used as a basis for estimating the total source populations in some of the major types of refinery process units. These estimated source populations are presented in Table 5-16. Sources were not counted in some types of process units including vacuum distillation, aromatics extraction, delayed coking, hydrodealkylation, and sulfur recovery units. The number of sources in these units were estimated from source counts obtained in other types of units.

An estimate of the number of valves, pump seals, and compressor seals in various process stream services is required to develop total hydrocarbon emission rates from refinery process units. These source distributions were determined for pumps and compressors during the field sampling program in refineries. Stream service distributions were not established for valves, however. Thus, the valve distributions were estimated by indirect means. The method is described in Appendix B (Volume 3).

The estimated distribution of pump seals and valves in selected refinery process units is given in Table 5-17.

5.2 Nonbaggable Source Measurements and Results

The nonbaggable sources that were sampled included cooling towers, API separators, corrugated plate interceptors, and dissolved air flotation units. Other potential nonbaggable emission activities such as spills, turnarounds, blind changing, coking operations, and air blowing were not sampled. The emission potentials of some of these activities were evaluated by surveys. The results are summarized in Section 6 of this report.

TABLE 5-16. ESTIMATED NUMBER OF INDIVIDUAL EMISSION SOURCES[2] IN 15 SPECIFIC REFINERY PROCESS UNITS

Process Unit	Estimated Number of Sources Within Battery Limits of Process Units					
	Valves	Flanges	Pumps[3]	Compressors[4]	Drains	Relief Valves
Atmospheric Distillation	890	3540	31	1	69	6
Vacuum Distillation[1]	500	2000	16	0[1]	35	6
Fuel Gas/Light Ends Processing	180	760	3	2	11	6
Catalytic Hydroprocessing	650	2600	10	3	24	6
Catalytic Cracking	1310	5200	30	3	65	6
Hydrocracking	930	3760	22	3	58	6
Catalytic Reforming	690	2760	14	3	49	6
Aromatics Extraction[1]	600	2400	18[1]	0[1]	41	6
Alkylation	680	2280	11	0	41	6
Delayed Coking[1]	300	1240	9[1]	0[1]	28	6
Fluid Coking	300	1240	9	4	28	6
Hydroealkylation[1]	690	3760	14[1]	3[1]	58	6
Treating/Dewaxing	600	2290	18	1	44	6
Hydrogen Production	180	640	5	3	17	4
Sulfur Recovery[1]	200	800	6[1]	0[1]	20	4

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[1] Sources were not counted in process units of this type. The number of sources was estimated.

[2] Only those sources in hydrocarbon (or organic compound) service.

[3] Number of pump seals = 1.4 x number of pumps.

[4] Number of compressor seals = 2.0 x number of compressors.

TABLE 5-17. AVERAGE NUMBER AND ESTIMATED DISTRIBUTION OF VALVE AND PUMP SEALS IN REFINERY PROCESS UNITS

	Average No. of Valves	Average No. of Pumps	Average No. of Compressors	Valve To Pump Ratio	Pump Service Distribution		Estimated Distribution of Valves, Number/Unit			Estimated Distribution of Pump Seals, Number/Unit		
					Light Liquid Service, %	Heavy Liquid Service, %	Gas Service	Light Liquid Service	Heavy Liquid Service	Light Liquid Service	Heavy Liquid Service	Total Pump Seals
Atmospheric Distillation	893	31	1	29	35	65	90	281	522	15	28	43
Vacuum Distillation	500[1]	16[1]	0[1]	34	10	90	55[1]	50[1]	945[1]	2[1]	19[1]	21[1]
Fuel Gas/Light Ends Processing	181	3	2	60	83	17	88	77	16	4	0	4
Catalytic Hydroprocessing	645	10	3	65	67	33	335	208	102	9	5	14
Catalytic Cracking	1314	30	3	44	44	56	384	409	521	18	24	42
Hydrocracking	931	22	3	42	55	45	250	375	306	17	14	31
Catalytic Reforming	691	14	3	49	90	10	260	388	43	18	2	20
Aromatics Extraction	600[1]	18[1]	0[1]	33	0.90[1]	0.10[1]	60[1]	486[1]	54[1]	15[1]	2[1]	17[1]
Alkylation	571	11	0	52	100	0	230	341	0	15	0	15
Delayed Coking	300[1]	9[1]	0[1]	33	21[1]	79[1]	30[1]	57[1]	213[1]	3[1]	10[1]	13[1]
Fluid Coking	304	9	4	34	21	79	30	58	216	3	10	13
Hydrodealkylation	700[1]	14[1]	3[1]	50	90[1]	10[1]	266[1]	391[1]	43[1]	18[1]	2[1]	20[1]
Dewaxing/Treating	599	18	1	33	39	61	60	210	329	11	18	29
Hydrogen Production	182	5	3	36	60	40	27	93	62	5	3	8
Sulfur Recovery	200[1]	6[1]	0[1]	33	84[1]	16[1]	90[1]	90[1]	20[1]	8	2	10

[1] Source counts were not made in the field. These values are estimated.

5.2.1 Cooling Tower Emissions Measurements

Hydrocarbon emissions from cooling towers were determined from hydrocarbon material balances around each tower. The hydrocarbon content of the incoming and outgoing water streams were determined by a total organic carbon (TOC) analysis and/or by a volatile organic purging procedure. Both of these methods are described in Section 4 of this report. A more detailed description of the sampling and analytical techniques are included in Appendix A (Volume 2). Calculation methods and complete measurement data are contained in Appendix B (Volume 3).

Thirty-one cooling towers were sampled. Eight of these had statistically significant emissions. The estimated emissions from the individual cooling towers are presented in Table 5-18. Streams from five towers were analyzed by both TOC and purge analyses. Thus, streams from a total of 21 towers were analyzed by TOC and streams from 15 towers were analyzed with the purging technique. An analysis of the results from both these analytical methods indicated that the purging technique was more accurate and precise than the TOC analysis. Where both analytical techniques were used, the results with the purging technique were chosen for calculation purposes.

The results of the cooling tower sampling program are presented in Table 5-19. Because the purge method of analysis was found to be the more precise method, an emission factor of 0.00011 lb/1000 gallons of circulating cooling water was developed using only the purge method results from the fifteen towers. A 95 percent confidence interval for this factor ranges from negligible to 0.0004 lb/1000 gallons.

5.2.2 Wastewater Systems

API separators, corrugated plate interceptors, and dissolved air flotation (DAF) units were sampled to determine atmospheric emissions of hydrocarbon. The emissions were estimated from a hydrocarbon material

TABLE 5-18. ESTIMATED EMISSIONS FOR INDIVIDUAL TOWERS

Tower Number	Analysis Method	Average Δ PPM	Standard Deviation	Student t Test	Circulation (GPM)	Blowdown (GPM)	Emissions (lb/hr)
1	Purge	0.002	0.020	0.24	1,000		
2	Purge	0.018	0.015	2.00	5,000		
3	TOC	0.35	2.49	0.24	58,000	155.0	
	Purge	0.061	0.139	0.87	58,000	155.0	
4	TOC	2.14	1.63	2.63**	5,250	28.5	6.47±4.44
5	TOC	1.25	1.53	1.82**	5,000	10.0	3.73±3.27
6	TOC	-1.17	1.82	-1.43	5,500	15.7	
7	TOC	1.61	2.12	1.86**	5,900	12.5	5.56±5.24
8	TOC	0.61	1.46	1.03	6,900	24.8	
9	TOC	0.38	3.69	0.23	9,000		
10	TOC	-5.03	7.53	-1.16	1,800	30.0	
	Purge	-0.008	0.046	-0.35	1,800	30.0	
11	TOC	10.09	10.49	2.35**	714	1.4	4.30±3.20
12	TOC	0.29	2.19	0.32	6,200	23.3	
13	TOC	3.94	1.63	4.83**	3,597	9.7	8.46±3.15
14	Purge	0.015	0.035	0.84	2,850		
15	Purge	0.034	0.016	4.36**	21,150		0.36±0.18
16	TOC	-0.14	1.37	-0.20	25,000		
17	TOC	0.83	1.57	1.19	6,700	14.3	
18	Purge	0.013					
19	TOC	-0.03	0.72	-0.10	3,900	15.4	
20	TOC	2.22	3.79	1.17	48,000	131.7	
	Purge	0.131	0.090	2.92**	48,000	131.7	3.14±2.32
21	TOC	1.45	0.70	3.61**	3,500		3.03±1.56
22	Purge	0.019					
23	TOC	1.46	2.68	1.09	5,000	50.0	
	Purge	-0.155	0.324	-0.96	5,000	50.0	
24	TOC	-0.80	1.26	-1.42	10,000	16.9	
25	TOC	3.45	4.96	1.20	15,000	106.7	
26	Purge	-0.025	0.045	-0.94	15,000	106.7	
26	Purge	0.016	0.037	0.88	29,600		
27	Purge	0.006					
28	Purge	0.011					
29	Purge	0.024					
30	TOC	-2.09	3.05	-1.67	8,570	17.1	
31	TOC	-0.24	1.64	-0.36	8,300	106.0	

**Statistically significant

TABLE 5-19. SUMMARY OF COOLING TOWER EMISSIONS

Cooling Towers Sampled		31
Cooling Towers Having Statistically Significant Emissions		8
Range of Cooling Tower Circulation Rates		714 to 58,000 GPM
	Results (estimate with 95% confidence interval)	
Mean Cooling Tower Δ HC Concentration		
From Emitting Towers		
Both Analyses	0.101 ± 0.19 ppm	(negligible, 0.29 ppm)
From All Towers Sampled		
TOC Analysis	1.25 ± 1.24 ppm	(0.01, 2.5 ppm)
Purge Analysis	0.0130 ± 0.0299 ppm	(negligible, 0.043 ppm)
Both Analyses[a]	0.0173 ± 0.058 ppm	(negligible, 0.075 ppm)
Mean Cooling Tower Emissions		
From Emitting Towers		
Both Analysis	0.00088 ± 0.0016 lb/1000 gal	(negligible, 0.0025 lb/1000 gal)
From All Towers Sampled		
TOC Analysis	0.0124 ± 0.0123 lb/1000 gal	(0.0001, 0.025 lb/1000 gal)
Purge Analysis	0.000108 ± 0.00025 lb/1000 gal	(negligible, 0.00036 lb/1000 gal)
Both Analyses[a]	0.000151 ± 0.00051 lb/1000 gal	(negligible, 0.00066 lb/1000 gal)
Range of Measurable Emissions	0.36 to 8.46 lb/hr	

[a] Calculated for 15 towers analyzed by TOC only plus 16 towers analyzed by purge. The 5 towers analyzed by both methods were represented only by the purge values, considered more accurate than TOC values.

balance around each unit. The methods used to determine the hydrocarbon content of the oil and water streams are described in Section 4 of this report. The methods are described in greater detail in Appendix A (Volume 2).

The results of the sampling program are presented in Table 5-20. There is a great deal of scatter and uncertainty in the data and results, particularly in the determination of emissions from the oil phase of the oil-water separators. Negative values are even indicated for some emissions. The one conclusion that can be made regarding these results is that the material balance approach, as implemented in this program, is inadequate for defining emission rates from oil-water separators. The composition of the incoming stream varies widely, and grab samples are not generally representative. For this reason, emission factors for oil-water separators were not developed from experimental results.

Emission measurements for dissolved air flotation (DAF) units were obtained from four different units using a material balance on the water phase only. The oily froth was not considered in the material balance. Emissions from the four water-phase units averaged 0.05 lb/1000 gallons of wastewater. The 95 percent confidence interval about the average value was from negligible to 0.24 lb/1000 gallons of wastewater. The DAF data were insufficient to allow the development of an emission factor which can be used with confidence.

5.3 Stack Emissions

The results of sampling FCCU regenerator stacks, heater stacks, sulfur recovery/tail gas treating unit stacks, and other miscellaneous stacks are summarized in the sections below.

TABLE 5-20. DESCRIPTION OF SAMPLED DEVICES - WASTE OIL/WATER SYSTEMS

Refinery	Device	Covered/Uncovered	Average Hydrocarbon Emissions	
			Losses from Oil Phase, lb/gal slop oil	Losses from Water Phase, lb/gal water
1	R Rectangular API Separator	C	1.6 ± 2	$2.7\times10^{-4} \pm 1.8\times10^{-4}$
	Circular DAF	U		$8.2\times10^{-5} \pm 1.5\times10^{-4}$
2	Rectangular API Separator	C	1.84 ± 1.11	$-3.01\times10^{-6} \pm 1\times10^{-5}$
3	Corrugated Plate Interceptor	C	-1.5 ± 0.08	--
	Corrugated Plate Interceptor	C	-0.11 ± 0.06	--
4	Rectangular API Separator Forebay Covered	U	0.12 ± 1.3	$2.2\times10^{-4} \pm 2.7\times10^{-4}$
5	Surge Tank	U	0.45	
	Two Rectangular Separators	U	--	$1.6\times10^{-5} \pm 3\times10^{-6}$
	Rectangular DAF	U	--	$-2.4\times10^{-5} \pm 2.7\times10^{-5}$
6	Rectangular API Separator	U	-1.1 ± 0.74	$1.5\times10^{-4} \pm 2.4\times10^{-4}$
7	Rectangular API Separator	U	0.14 ± 0.4	$6.5\times10^{-4} \pm 1.9\times10^{-4}$
	Rectangular DAF	U	--	$1.1\times10^{-4} \pm 1.3\times10^{-4}$
8	Circular Separator	U	0.48 ± 0.61	$3.4\times10^{-4} \pm 1.8\times10^{-4}$
	Circular DAF	U	--	$1.4\times10^{-5} \pm 1.7\times10^{-5}$

5.3.1 FCCU Regenerator Stack Measurements

A total of seven stacks from five different FCCU's were sampled for criteria pollutants and individual organic species. The results of the sampling are presented in Tables 5-21 through 5-23. The FCCU regenerator stacks included in Table 5-21 were all equipped with electrostatic precipitators and CO boilers. Stacks No. 13 and 18 were from separate CO boilers on the same FCCU.

The results shown in Table 5-22 were obtained from an FCCU whose flue gases passed through a CO boiler and then through a scrubber. Two scrubber units each handled approximately one-half of the flue gas. Both particulates and SO_x were removed in the scrubbers.

In only one case were samples obtained upstream of the CO boiler and/or ESP. The results are shown in Table 5-23. Only grab samples could be be taken upstream of the control devices. The CO boiler was effective in removing the organic species such as aldehydes and HCN.

In Table 5-24, the FCCU regenerator emissions are expressed as functions of the fresh feed rate to the FCC units. Although data are limited on the effectiveness of the scrubbers, they appeared to be somewhat more effective than electrostatic precipitators in reducing particulate emissions. The level of SO_x in the flue gases was quite low in the two FCCU scrubber stacks.

5.3.2 Crude Unit Process Heater Stack Measurements

Process heater stacks from five crude oil distillation units were sampled. The results are summarized in Tables 5-25 and 5-26. Detailed data are given in Appendix B (Volume 3).

TABLE 5-21. RESULTS OF SAMPLING FLUE GASES FROM FCCU REGENERATORS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS AND CO BOILERS

Species	CO Boiler Stack No. 11		CO Boiler Stack No. 14		CO Boiler Stack No. 16		CO Boiler Stack No. 13[a]		CO Boiler Stack No. 18[a]	
	ppmv[b]	lb/scf	ppmv[b]	lb/scf	ppmv[b]	lb/scf	ppmv[b]	lb/scf	ppmv[b]	lb/scf
Aldehydes (as Formaldehyde)	0.066	5.12×10^{-9}	10.0	7.76×10^{-7}	6.70	5.19×10^{-7}	7.30	5.66×10^{-7}	5.54	4.30×10^{-7}
Methane Hydrocarbons	0.602	2.49×10^{-8}	2.36	9.75×10^{-8}	0.0	0.0	ND	ND	ND	ND
Nonmethane Hydrocarbons (as Hexane)	16.1	3.57×10^{-6}	9.51	2.11×10^{-6}	2.61	5.79×10^{-7}	3.80	8.44×10^{-7}	1.91	4.24×10^{-7}
Particulates	(0.184)[c]	2.63×10^{-5}	U	U	(0.0154)[c]	2.20×10^{-6}	(0.0426)[c]	6.09×10^{-6}	(0.0493)[c]	7.04×10^{-6}
SO_2	96.8	1.60×10^{-5}	625	1.03×10^{-4}	13.4	2.22×10^{-6}	406.6	6.725×10^{-5}	327.3	5.414×10^{-5}
SO_3	8.30	1.72×10^{-6}	7.27	1.50×10^{-6}	1.15	2.37×10^{-7}	1.14	2.35×10^{-7}	1.89	3.91×10^{-7}
H_2S	U[d]	U	ND	ND	<0.10	$<8.79 \times 10^{-9}$	0.58	5.12×10^{-8}	ND	ND
COS	ND[e]	ND	ND	ND	0.067	1.03×10^{-8}	ND	ND	ND	ND
CS_2	ND	ND	U	U	<0.067	$<1.31 \times 10^{-8}$	0.40	7.86×10^{-8}	1.33	2.61×10^{-7}
NO_x (as NO_2)	U	U	184.9	2.20×10^{-5}	415.3	4.938×10^{-5}	257.7	3.064×10^{-5}	225.0	2.675×10^{-5}
HCN	0.80	5.58×10^{-8}	1.03	7.19×10^{-8}	0.204	1.42×10^{-8}	0.012	8.37×10^{-10}	0.005	3.49×10^{-10}
NH_3	0.87	3.81×10^{-8}	0.73	3.19×10^{-8}	<4.25	$<1.87 \times 10^{-7}$	0.216	1.48×10^{-8}	ND	ND
Total Gas Flow Rate, SCFM	2.70×10^6		1.26×10^6		8.97×10^6		9.15×10^6		8.58×10^6	

[a] CO boilers in same FCC unit.

[b] Dry basis.

[c] Given as grains/SCF.

[d] U = Undetermined.

[e] ND = Not detected.

TABLE 5-22. RESULTS OF SAMPLING FLUE GASES FROM FCCU REGENERATORS EQUIPPED WITH CO BOILERS AND SCRUBBERS

Species	FCCU CO Boiler Scrubber-Stack No. 12[a]		FCCU CO Boiler Scrubber-Stack No. 17[a]	
	ppmv[b]	lb/SCF	ppmv[b]	lb/SCF
Aldehydes (as Formaldehyde)	46.3	3.59×10^{-6}	36.1	2.80×10^{-6}
Methane Hydrocarbons	89.4	3.70×10^{-6}	14.3	5.92×10^{-7}
Nonmethane Hydrocarbons (as Hexane)	28.3	6.28×10^{-6}	12.7	2.83×10^{-6}
Particulates	(0.019)[c]	2.71×10^{-6}	(0.024)[c]	3.43×10^{-6}
SO_2	5.13	8.49×10^{-7}	12.5	2.07×10^{-6}
SO_3	0.16	3.31×10^{-8}	0.35	7.24×10^{-8}
H_2S	U[d]	U	U	U
COS	U	U	U	U
CS_2	U	U	U	U
NO_x (as NO_2)	41.1	4.89×10^{-6}	180.8	2.15×10^{-5}
HCN	U	U	U	U
NH_3	U	U	U	U
Total Gas Flow Rate, SCFM	9.08×10^{6}		8.53×10^{6}	

[a] Both scrubbers located on same unit.

[b] Dry basis.

[c] Given as grains/SCF.

[d] U = Undetermined.

TABLE 5-23. RESULTS OF SAMPLING FCCU REGENERATOR FLUE GAS UPSTREAM AND DOWNSTREAM OF CO BOILER/ESP[a]

Species	Species Concentration Upstream of CO Boiler and ESP		Species Concentration Downstream of CO Boiler (Stack No. 15)	
	ppmv [a]	lb/SCF	ppmv [a]	lb/SCF
Aldehydes (as Formaldehyde)	208	1.61×10^{-5}	17.2	1.33×10^{-6}
Methane Hydrocarbons	U[c]	U	U	U
Nonmethane Hydrocarbons (as Hexane)	U	U	U	U
Particulates	U	U	(0.0686)[d]	9.80×10^{-6}
SO_2	332.5	5.50×10^{-5}	677	1.12×10^{-4}
SO_3	U	U	0.954	1.97×10^{-7}
H_2S	U	U	U	U
COS	U	U	U	U
CS_2	U	U	U	U
NO_x (as NO_2)	41.5	4.93×10^{-6}	100	1.19×10^{-5}
HCN	109.5	7.64×10^{-6}	19.1	1.33×10^{-6}
NH_3	3.99	1.75×10^{-7}	11.0	4.83×10^{-7}
Total Gas Flow Rate, SCFM	U		6.53×10^{6}	

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[a] Flue gas from FCCU regenerator passed through an ESP and into the CO boiler; samples were obtained prior to the ESP and from the CO boiler stack.

[b] Dry basis.

[c] U = Undetermined.

[d] Given as grains/SCF.

TABLE 5-24. CONTROLLED EMISSION RATES FROM FLUID CATALYTIC CRACKING UNIT (FCCU) STACKS

Species	Control Devices in Use During Testing							
	CO Boiler, Scrubber	CO Boiler, Scrubber	ESP,[b] CO Boiler	ESP, CO Boiler	ESP, CO Boiler	ESP, CO Boiler	ESP, CO Boiler	ESP, CO Boiler
	Species Emission Rates, lb/1000 bbl Fresh Feed							
	Stack No. 12[a]	Stack No. 17[a]	Stack No. 15	Stack No. 11	Stack No. 13[c]	Stack No. 18[c]	Stack No. 14	Stack No. 16
Aldehydes (as Formaldehyde)	12	8	5	< 1	3	3	< 1	5
Methane	12	2		< 1	0	0	< 1	0
Nonmethane Hydrocarbons (as Hexane)	20	9	--	5	5	2	1	5
Particulate Matter	9	10	33	36	34	37	--	20
SO_2	3	6	381	22	378	286	46	20
SO_3	0.1	0.2	0.7	2.3	1.3	2.1	0.7	2.1
H_2S	--	--	--	--	0.3	0	0	< 0.1
COS	--	--	--	0	0	0	0	0.09
CS_2	--	--	--	0	0.4	1.4	--	< 0.1
NO_x (as NO_2)	16	65	41	--	173	141	10	443
HCN	--	--	4.5	0.1	0.005	0.002	0.03	0.13
NH_3	--	--	1.7	0.1	0.07	0	0.01	< 1.7
TOTAL Gas Flow, SCFH	9.08×10^6	8.53×10^6	6.53×10^6	2.70×10^6	9.15×10^6	8.58×10^6	1.26×10^6	8.97×10^6

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[a] Approximate emission rates. Stacks No. 12 and 17 were located on the same unit. The feed rate to the FCCU was equally divided between the two stacks for the purpose of calculating emission rates.

[b] ESP = electrostatic precipitator.

[c] Approximate emission rates. FCCU had two CO boilers, Stacks No. 13 and No. 18. The feed rate to the FCCU was equally divided between the two boilers for the purpose of calculating emissions rates.

TABLE 5-25. RESULTS OF SAMPLING FLUE GASES FROM CRUDE UNIT PROCESS HEATERS

Species	Stack No. 2		Stack No. 3		Stack No. 4		Stack No. 5		Stack No. 6	
	ppmv[a]	lb/SCF	ppmv[a]	lb/SCF	ppmv[a]	lb/SCF	ppmv[a]	lb/SCF	ppmv[a]	lb/SCF
Aldehydes (as Formaldehyde)	6.62	5.13×10^{-7}	6.84	5.30×10^{-7}	0.047	3.62×10^{-9}	0.11	8.53×10^{-9}	8.93	6.92×10^{-7}
Methane Hydrocarbons	0.0	0.0	0.029	1.18×10^{-9}	0.46	1.88×10^{-8}	2.67	1.14×10^{-7}	0.45	1.86×10^{-8}
Nonmethane Hydrocarbons (as Hexane)	0.77	1.72×10^{-7}	0.88	1.96×10^{-7}	1.07	2.37×10^{-7}	6.26	1.39×10^{-6}	1.80	3.99×10^{-7}
Particulates	(0.042)[b]	5.94×10^{-6}	(0.038)[b]	5.40×10^{-6}	(0.064)[b]	9.07×10^{-6}	U[c]	U	U	U
SO_2	2.15	3.56×10^{-7}	1.06	1.75×10^{-7}	295.5	4.89×10^{-5}	95.7	1.58×10^{-5}	0.18	2.98×10^{-8}
SO_3	0.61[a]	1.25×10^{-7}	0.15	3.02×10^{-8}	0.72	1.49×10^{-7}	21.2	4.38×10^{-6}	U	U
H_2S	U	U	U	U	U	U	U	U	ND[d]	ND
COS	U	U	U	U	U	U	U	U	ND	ND
CS_2	U	U	U	U	U	U	U	U	ND	ND
NO_x (as NO_2)	U	U	U	U	U	U	U	U	92.9	1.10×10^{-5}
HCN	<0.021	$<1.49 \times 10^{-9}$	<0.001	$<6.98 \times 10^{-11}$	U	U	0.85	5.93×10^{-8}	U	U
NH_3	<0.30	$<1.32 \times 10^{-8}$	<0.30	$<1.32 \times 10^{-8}$	U	U	1.23	5.40×10^{-8}	U	U
Total Gas Flow Rate, SCFM	3.26×10^{6}		2.34×10^{6}		7.03×10^{6}		2.78×10^{6}		U	

[a] Dry basis.

[b] Given as grains/SCF.

[c] U = Undetermined.

[d] ND = Not detected.

TABLE 5-26. COMPOSITION OF REFINERY HEATER STACK GAS

Species	Stack Gas Composition, Parts per million by Volume (ppmv)[a]				
	Stack No. 2	Stack No. 3	Stack No. 4	Stack No. 5	Stack No. 6
Aldehydes (as Formaldehyde)	6.6	6.8	0.05	0.1	8.9
Methane Hydrocarbons	0.0	0.0	0.5	2.7	0.5
Nonmethane Hydrocarbons (as Hexane)	0.8	0.9	1.1	6.3	1.8
Particulate Matter	(0.042)[b]	(0.038)	(0.064)	U[e]	U
SO_2	2.2	1.1	296	96	0.2
SO_3	0.6	0.2	0.72	21	U
H_2S	U[d]	U[d]	U	U	ND[c]
COS	U	U	U	U	ND
CS_2	U	U	U	U	ND
NO_x (as NO_2)	U	U	U	U	93
HCN	< 0.021	< 0.001	U	0.9	U
NH_3	< 0.030	< 0.3	U	1.2	U
TOTAL Gas Flow Rate, SCFM	3.26×10^6	2.34×10^6	7.03×10^6	2.78×10^6	U

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[a] Dry basis

[b] Expressed as grains/SCF

[c] ND = not detected

[d] U = undetermined

[e] Nonisokinetic conditions, grain loading not reported

The process heaters were fired with mixed refinery fuel gas-fuel oil. No external emission controls were in use during any of the sampling activities.

5.3.3 Emissions From Tail Gas Treating Units

The stack gases from the tail gas treating processes of two sulfur recovery units were sampled and analyzed. The compositions of these gases are given in Table 5-27. The accuracy of the hydrocarbon and SO_x analyses of the gas from Stack No. 7 is uncertain. The concentration of hydrocarbons in the gas is very high. At the same time alnost no SO_2 was found. No satisfactory explanation of these results has been put forward.

5.3.4 Miscellaneous Source Emissions

Several miscellaneous source stacks were sampled. The results are summarized in Table 5-28. The flue gas from a fluid coker was sampled upstream and downstream of the control devices, a scrubber and a CO boiler. The effectiveness of the controls can be seen in Table 5-28. The table also contains data on a resin fume oxidation unit, a TCC regenerator and FCCU compressor engine (internal combustion) exhausts.

5.4 Identification of Emitted Species

The characterization and measurement of organic emissions from controlled and uncontrolled sources were conducted at several petroleum refineries. The controlled sources from which samples were taken and analyzed include FCCU CO boiler stacks, TCC CO boiler stacks, fluid coker CO boiler stack and a fume oxidation unit.

Uncontrolled sources included valves, flanges, pump seals, compressor seals, and drains. Fugitive vapor emission samples and corresponding liquid samples were obtained in many cases. Vapor samples were obtained from leaking valves and pump seals. Corresponding liquid samples were obtained

TABLE 5-27. COMPOSITION OF STACK GAS FROM SULFUR RECOVERY TAIL GAS TREATING UNITS

Species	Species Concn. in Flue Gas, ppmv[a]	
	Stack No. 7	Stack No. 8
Aldehydes (as Formaldehyde)	U[b]	4.0
Methane Hydrocarbons	5870	0.8
Nonmethane Hydrocarbons(as Hexane)	2080	5.7
SO_2	0.2	460
SO_3	U	0.7
H_2S	U	ND[d]
COS	6.4	0.5
CS_2	9.0	1.9
NO_x (as NO_2)	15.0	16.7
HCN	U	< 0.001
NH_3	U	< 0.03
TOTAL Gas Flow, SCFM	U	(2.02×10^5)[c]

[a] Dry Basis

[b] U = undetermined

[c] Provided by plant personnel

[d] ND = not detected

TABLE 5-28. MISCELLANEOUS STACK EMISSIONS

Process Unit:	Fluid Coking Unit		Resin Fume Oxidation Unit	TCC Unit Regenerator	FCCU Compressor Engine Exhaust
Gas Stream:	Scrubber Inlet	CO Boiler Outlet	Flue Gas	Flue Gas	Exhaust Gas
Control Devices in Use During Tests:	Scrubber, CO Boiler		--	CO Boiler	--
Species	Gas Composition, lb per 1000 bbl feed	Emission Rate, lb per 1000 bbl feed	Gas Composition, ppmv[a]	Emission Rate, lb per 1000 bbl feed	Gas Composition, ppmv[a]
Aldehydes (as Formaldehyde)	3.2	1.3	34	2.3	U
Methane Hydrocarbons	933	3.7	1.5	0.0	4.0
Nonmethane Hydrocarbons (as Hexane)	135	12.7	2.3	0.2	72
Particulate Matter	437	153	(0.0063)[b]	15	(0.042)[a]
SO_2	ND[c]	267	18	321	0.50
SO_3	ND	1.4	0.4	0.5	0.61
H_2S	ND	ND	ND[c]	U	U
COS	ND	ND	ND	U	U
CS_2	ND	ND	ND	U	U
NO_x (as NO_2)	7.1	159	U[d]	43	U
HCN	36.9	1.2	U	ND	2.1
NH_3	35.3	0.2	U	0.3	1.4
TOTAL Gas Flow Rate, SCFH	1.77×10^6	2.44×10^6	3.09×10^5	3.10×10^6	0.55×10^6

[a] Dry basis

[b] Expressed as grains/SCF

[c] ND = not detected

[d] U = undetermined

from liquid process streams at locations as near as possible to the vapor sample point. Both the liquid and vapor samples were analyzed. Details of the sampling and analyses procedures are described in detail in Appendix A (Volume 2). They are summarized in Section 4 of this report.

The collection and analysis of vapor samples is time consuming. The collection and analysis of liquid samples is much simpler. Laboratory experiments were conducted to determine the relationship between fugitive vapor composition and the corresponding process liquid composition. These experiments indicated that the composition of fugitive emissions from refinery equipment is identical to the composition of the liquid within the leaking source. (See Appendix B, Volume 3.) As a result of these experiments, liquid stream samples were preferentially analyzed, wherever possible, instead of the corresponding vapor samples.

The analyses were done by GC-MS. The analytical emphasis was placed on the identification and quantitation of aromatic and polynuclear aromatic compounds. The detailed results of these analyses are presented in Appendix B (Volume 3). For brevity, the results are only summarized here.

5.4.1 Species Present in FCCU Regenerator Flue Gas

Particulate matter in the flue gas was collected by cyclones in a Source Assessment Sampling System (SASS) train. Fine particulates were collected on a filter downstream of the cyclones. The sampled gas also passed through a cannister packed with adsorbent to collect volatile organic compounds. The organic material present on or in the particulate matter was extracted and subjected to GC-MS analysis. The organic material on the adsorbent was similarly analyzed.

Individual species found and identified in particulate matter and/or adsorbed material are listed in Table 5-29. A total of seven particulate and seven adsorbed vapor samples were analyzed. Those species other

TABLE 5-29. ORGANIC SPECIES FOUND IN FCCU FLUE GAS SAMPLES[a,b]

Organic Compounds[c] Present at Concentrations >0.1 ppb
Anthracene/phenanthrene
Methylanthracene/phenanthrene
Naphthalene
Methylnaphthalenes
C_2-naphthalenes
Benzoic acid
Biphenyl
Cresol
Cyclohexane diol
Cyclohexanol
Cyclohexanone
Cyclohexene oxide
Methylcyclohexanone
Benzaldehyde
Acenaphthene
Acenaphthylene
Benz(a)anthracene/chrysene
C_2-alkylphenols
C_3-alkylphenols
Dibenzofuran
Fluorene
Fluoranthene
Indanol
Methylphenols
Nonylphenol
Octylphenol

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[a] Species found in particulate matter and/or vapor samples.
[b] C_n-C_{31} alkanes detected but not listed.
[c] All samples were taken downstream of CO boilers and ESP or scrubber.

than alkanes which were found in any of the samples at concentrations above 0.1 ppb are listed. Alkanes were present, but they are not listed.

Particulate samples from two FCCU were subjected to an elemental analysis. The results are shown in Tables 5-30 and 5-31.

5.4.2 Identification of Organic Compounds in Fugitive Vapor Samples

Some samples of hydrocarbon vapors from leaking valves and pump seals were collected in canisters packed with adsorbent. However, laboratory experiments indicated that the composition of liquid streams inside a leaking source was the same as that of the emitted vapor. The analysis of liquid samples was less time-consuming and more economical. Thus, most of the sampled material is liquid from process lines.

The sampled stream types are listed in Table 5-32. The organic compounds which were detected in the vapor samples or which were found in concentrations above 10 ppm in liquid samples are listed in Table 5-33.

5.4.3 Potentially Hazardous Organic Species in Sampled Refinery Streams

The results of the detailed analyses of vapor and liquid samples taken from refinery process streams and emission points are summarized in this section. Only those organic species which are potentially the most hazardous of those which might be present in refinery streams are considered. These species and their concentration ranges which were found in process streams are presented in Tables 5-34 and 5-36. The stream identification numbers and descriptions are given in Table 5-35.

TABLE 5-30. ELEMENTAL ANALYSIS OF FCCU CO BOILER FLUE GAS PARTICULATES (STACK A)

Element	Conc.[a]	Element	Conc.	Element	Conc.	Element	Conc.
Uranium	5	Terbium	29	Ruthenium	--	Vanadium	150
Thorium	6	Gadolinium	150	Molybdenum	66	Titanium	MC
Bismuth[b]	--	Europium	14	Niobium	15	Scandium	17
Lead	54	Samarium	490	Zirconium	48	Calcium	MC
Thallium	--	Neodymium	MC[c]	Yttrium	240	Potassium	MC
Mercury	--	Praseodymium	MC	Strontium	120	Chlorine	22
Gold	--	Cerium	MC	Rubidium	≤0.5	Sulfur	MC
Platinum	--	Lanthanum	MC	Bromine	≤3	Phosphorus	MC
Iridium	--	Barium	790	Selenium	36	Silicon	MC
Osmium	--	Cesium	0.2	Arsenic	4	Aluminum	MC
Rhenium	--	Iodine	--	Germanium	≤0.7	Magnesium	MC
Tungsten	5	Tellurium	--	Gallium	10	Sodium	MC[c]
Tantalum	≤1	Antimony	0.9	Zinc	260	Fluorine	MC
Hafnium	3	Tin	5	Copper	40	Oxygen	NR[d]
Lutetium	1	Indium	STD[e]	Nickel	300	Nitrogen	NR
Ytterbium	5	Cadmium	≤0.5	Cobalt	50	Carbon	NR
Thulium	0.9	Silver	0.5	Iron	MC	Boron	69
Erbium	22	Palladium	--	Manganese	300	Beryllium	1
Holmium	24	Rhodium	--	Chromium	840	Lithium	280
Dysprosium	230					Hydrogen	NR

[a] Concentration in ppm by weight.

[b] Concentrations < 0.2 ppmw were not listed.

[c] MC - major component (70.1%).

[d] NR - not reported.

[e] STD - analytical method

TABLE 5-31. ELEMENTAL ANALYSIS OF FCCU CO BOILER FLUE GAS PARTICULATES (STACK C)

Element	Conc.[a]	Element	Conc.	Element	Conc.	Element	Conc.
Uranium	5	Terbium	7	Ruthenium	--	Vanadium	100
Thorium	19	Gadolinium	94	Molybdenum	150	Titanium	MC[c]
Bismuth [b]	--	Europium	9	Niobium	80	Scandium	12
Lead	29	Samarium	930	Zirconium	260	Calcium	MC
Thallium	--	Neodymium	MC $\simeq$ .4%	Yttrium	88	Potassium	MC
Mercury	NR	Praseodymium	MC $\simeq$ .3%	Strontium	130	Chlorine	150
Gold	--	Cerium	MC $\simeq$ 2%	Rubidium	$\leq$ 8	Sulfur	MC
Platinum	--	Lanthanum	MC $\simeq$ 4%	Bromine	$\leq$ 3	Phosphorus	MC
Iridium	--	Barium	860	Selenium	5	Silicon	MC
Osmium	--	Cesium	1	Arsenic	4	Aluminum	MC
Rhenium	--	Iodine	0.4	Germanium	$\leq$ 1	Magnesium	200
Tungsten	2	Tellurium	--	Gallium	53	Sodium	MC
Tantalum	1	Antimony	3	Zinc	130	Fluorine	MC
Hafnium	4	Tin	4	Copper	140	Oxygen	NR[d]
Lutetium	0.4	Indium	STD[e]	Nickel	550	Nitrogen	NR
Ytterbium	2	Cadmium	$\leq$0.3	Cobalt	60	Carbon	NR
Thulium	0.6	Silver	$\leq$0.3	Iron	MC	Boron	8
Erbium	12	Palladium	--	Manganese	680	Beryllium	0.3
Holmium	10	Rhodium	--	Chromium	MC	Lithium	11
Dysprosium	30					Hydrogen	NR

[a] Concentration in ppm by weight.

[b] Concentrations < 0.2 ppmw were not listed.

[c] MC - major component (>0.1%).

[d] NR - not reported.

[c] STD - analytical standard.

TABLE 5-32. SAMPLED REFINERY HYDROCARBON STREAMS

Gas Streams

- Reformer Recycle Hydrogen
- Atmospheric Crude Distillation: Overhead Gas
- FCCU Low Pressure Separator Gas

Liquid Streams

- Atmospheric Crude Distillation:
  - Intermediate Naphtha
  - Full Range SR Gasoline
  - Virgin Distillate
  - Atmospheric Gas Oil
- Vacuum Distillation:
  - Light Vacuum Gas Oil
  - Vacuum Gas Oil
  - Heavy Vacuum Gas Oil
  - Vacuum Residuum
- Reforming:
  - Naphtha to Feed Hydrotreating
  - Naphtha to Reformer
  - Reformate
- FCCU:
  - Reflux Accumulator Bottoms
  - Separator Bottoms
  - Main Fractionator Overhead Liquid
  - Light Cycle Gas Oil
  - Heavy Cycle Gas Oil
- Desulfurized Naphtha
- Desulfurized Gas Oil
- Alkylation:
  - Reactor Product
  - Crude Alkylate
- TCC: Heavy Cycle Gas Oil
- Absorber Lean Oil
- Slack Wax from Dewaxing
- API Separator:
  - Inlet Oil
  - Surface Oil
  - Skimmed Oil

TABLE 5-33. ORGANIC SPECIES PRESENT IN REFINERY LIQUID STREAMS AND EMITTED VAPORS[a]

C_n-C_{32} alkanes
Benzene
Toluene
Xylenes
Ethylbenzene
Trimethylbenzene
Diethylbenzene
Dimethylethylbenzene
Tetramethylbenzene
sec-butylbenzene
Naphthalene
Methylnaphthalenes
Biphenyl
C_2-alkylnaphthalenes
C_3-naphthalenes
Phenanthrene/anthracene
Methylphenanthrene/anthracene
C_2-alkylphenanthrene/anthracene
C_3-alkylphenanthrene/anthracene
Propylbenzene
Ethyltoluene
Methylisopropylbenzene
Methylpropylbenzene
Diethylbenzene
Dimethylethylbenzene
Indan
Methyl indan
C_5-alkylbenzene
Tetralin
Biphenyl
Methylbiphenyl
C_2-alkylbiphenyls
Fluorene
Methylfluorene
C_2-alkylfluorenes
Acenaphthene
Methylacenaphthene
C_4-alkylacenaphthene
C_2-alkylnaphthalenes
Dibenzothiophene
Methyldibenzothiophene
C_2-alkyldibenzothiophene
C_3-alkyldibenzothiophene
C_4-alkyldibenzothiophene
C_5-alkyldibenzothiophene
Fluoranthene
Pyrene
Methylfluoranthene/pyrene
C_2-alkylfluoranthene/pyrene
C_3-alkylfluoranthene/pyrene
C_4-alkylfluoranthene/pyrene
Naphthabenzothiophene
C_5-phenanthrene/anthracene
C_3-alkylchrysene/benzanthracenes

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[a] Listed compounds were detected in vapor samples or were present in liquid streams at concentrations of 10 ppm or greater.

TABLE 5-34. POTENTIALLY HAZARDOUS SPECIES IN VAPOR[a] SAMPLES FROM REFINERY STREAMS

	Potentially Hazardous Species Concentration in Vapor Samples From The Various Sampled Streams[b]		
	0.01 - 0.1 ppb	0.1 - 1.0 ppb	> 1.0 ppb
Benzene	—	—	—
Isopropylbenzene	—	—	—
Trimethyl benzenes	—	—	—
Naphthalene	1, 4	1, 2	1
Anthracene/Phenanthrene	1, 2, 3	1, 4	
Biphenyl	1, 3, 4	1, 2	—
Methyl naphthalene	2, 4	1	—
Perylene	—	—	—
Benzo(a)-pyrene	1	—	—
Benzo(e)-pyrene	—	—	—
Methylcholanthrene	—	—	—
Benzanthracenes	—	—	—
Pyrene	1, 2, 3, 4	1	—
Fluoranthene	1, 2, 4	—	—
Benzofluorenes	1	—	—
Benzo(ghi)-perylene	1	—	—
Acenaphthene	1	1	—
Fluorene	1, 2	—	—
Phenol	1	4	—
o, m, p-cresol	1, 4	1	—

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[a] Samples taken from leaking vapor or present on particulate matter from FCCU regenerator flue gas.

[b] See Table 5-35 for stream type identification.

TABLE 5-35. VAPOR AND LIQUID STREAM IDENTIFICATION NUMBER

Stream ID Number	Sample Phase	Stream Type Description
1	Vapor	FCCU CO Boiler Flue Gas
2	Vapor	Fluid Coker CO Boiler Flue Gas
3	Vapor	Resin Fume Oxidation Unit Flue Gas
4	Vapor	TCC CO Boiler Flue Gas
5	Liquid	API Separator - Inlet Oil
6	Liquid	API Separator - Surface Oil
7	Liquid	API Separator - Skimmed Oil
8	Liquid	Crude Oil Desalter Water
9	Liquid	Sour Water Stripper Feed (Water)
10	Liquid	Desulfurized Naphtha (from hydrodesulfurization)
11	Liquid	Intermediate range Naphtha from Atmospheric Distillation
12	Liquid	Naphtha to Hydrotreating (for Reformer Feed)
13	Liquid	Naphtha to Reforming
14	Liquid	Straight Run Gasoline from Atmospheric Distillation
15	Liquid	FCCU Reflux Accumulator Bottoms
16	Liquid	FCCU Separator Bottoms
17	Liquid	FCCU Main Fractionator Overhead
18	Liquid	Reformate
19	Liquid	Absorber Lean Oil
20	Liquid	Crude Alkylate (Alkylation Unit)
21	Liquid	Virgin Distillate from Atmospheric Distillation
22	Liquid	Desulfurized Gas Oil
23	Liquid	Atmospheric Gas Oil
24	Liquid	Light Vacuum Gas Oil
25	Liquid	FCCU Light Cycle Gas Oil
26	Liquid	FCCU Heavy Cycle Gas Oil
27	Liquid	TCC Unit Heavy Cycle Gas Oil
28	Liquid	Flashed Crude

TABLE 5-36. POTENTIALLY HAZARDOUS SPECIES IN REFINERY LIQUID STREAMS

Potentially Hazardous Compounds	Potentially Hazardous Species Concentration in Liquid Samples from the Various Hydrocarbon Streams[a]		
	10 - 100 ppm	100 - 10,000 ppm	> 10,000 ppm
Benzene	4, 5, 7, 10, 11, 14, 18, 27	5, 12, 13, 15, 16, 18, 19, 20, 26	--
Isopropylbenzene	4, 5, 10, 11, 14, 18	6, 7, 12, 13, 15, 18, 19, 20, 26	--
Trimethyl benzenes	24, 25, 26	4,5,6,7,10,11,12,13,14,18,19,20,21,26,27	15, 16, 17
1,2,3,4-tetrahydronaphthalene	--	--	--
Naphthalene	11, 14, 18, 19, 21, 24, 25, 26	4, 5, 7, 12, 18, 20, 26, 27	13, 15, 16, 17, 25
Anthracene/Phenanthrene	13, 21, 25	4, 5, 6, 7, 25, 26, 27	--
Biphenyl	18	4, 5, 6, 7, 13, 25	--
Methyl naphthalenes	11, 18, 24	4, 5, 7, 12, 18, 20, 21, 26	6, 13, 15, 16, 25
Perylene	--	--	--
Benzo(a)-pyrene	--	--	--
Benzo(e)-pyrene	--	--	--
Benzanthracenes	--	--	--
Pyrene	21	26, 27	--
Fluoranthene	21	--	--
Benzofluorenes	--	--	--
Benzo(ghi)-perylene	--	--	--
Coronene	--	--	--
Acenaphthene	21	6	--
Fluorene	4, 18, 21	5, 6, 7, 25, 27	--
Phenol	--	--	--
o, m, p-cresol	--	--	--

[a] See Table 5-35 for Stream Type Identification.

The species listed in Tables 5-34 and 5-36 met one or more of the following criteria:

- Threshold limit value (TLV) $\leq$ 5.0 ppmv
- Acute local inhalation rating of 3 (Materials which on a single exposure lasting seconds or minutes cause injury to mucous membranes of sufficient severity to threaten life or cause permanent physical impairment or disfigurement).[26]
- Acute systemic inhalation rating of 3 (Materials which can be absorbed into the body by inhalation and which can cause injury of sufficient severity to threaten life following a single exposure lasting seconds, minutes, or hours).[26]
- Known or suspected carcinogen.
- Detected by analyses in at least one sample.

The stream identification numbers may appear in more than one concentration range for a given species. Many stream types were sampled at several different refineries. The resulting analyses showed different concentration ranges for some species.

5.5 Quality Control

A comprehensive quality assurance program was an integral part of this program. The quality assurance program for the sampling and analysis activities included the following elements:

- Formatted data collection forms for direct keypunching of data recorded in the field.

- Repeated sampling of individual sources with the same and different sampling teams and sampling equipment.

- Sampling and subsequent analysis of standard gas mixtures.

- Continuous sample runs over an eight-hour period.

- Daily testing of screening devices on the same sources.

- Multiple screenings of the same devices by different engineers.

- Replicate sample analysis and blind standard analysis in the laboratory.

Some of the more important results of the quality assurance effort are summarized in this section of the report. A much more detailed description of the quality assurance program is presented in Appendix C (Volume 4) of this report.

5.5.1 Quality Control for Baggable Source Hydrocarbon Measurements

The quality control precedures for baggable source hydrocarbon emissions measurement include laboratory analyses of blind standards, repeated total hydrocarbon (THC) analyses, recovery studies of the sampling train, and reproducibility of the sampling/analysis from a given source.

5.5.1.1 Laboratory Standard Analyses

Regularly scheduled analyses of blind standards were used to evaluate the daily calibration of the Byron THC analyzer as well as the stability of the calibration. The percent differences between the known and the measured concentrations ranged from - 55 percent to + 13 percent. The average difference was - 1.75 percent with a standard deviation of 10 percent. The 95 percent confidence interval for the mean difference was - 4.7 percent to + 1.4 percent.

5.5.1.2 Replicate Analyses for Total Hydrocarbons

The precision of the nonmethane hydrocarbon analysis as determined with the Byron THC analyzer were determined from a statistical analysis of duplicate analyses made at each refinery. The following statistics summarize the results of the duplicate analyses:

Number of replicate pairs:	130
Pooled standard deviation:	2.4 %
Repeatability - maximum difference expected between 2 readings 95 % of the time:	6.2 %
95 % confidence interval for mean reading based on a single analysis:	± 4.8 %
95 % confidence interval for mean reading based on the average of two analyses:	± 3.4 %

Since the average of two analyses was used in computing leak rates for all sources, the ± 3.4 percent interval best describes the precision of the THC analysis.

5.5.1.3 Results of Recovery Studies

The overall accuracy of the baggable source sampling and analysis procedure was evaluated. Known leak rates were generated and measured. The percentage of the leaking material which was recovered in the sampling train was used as a measure of overall accuracy. Sixty-three recovery studies were made at nine of the visited refineries. The induced leak rates ranged from 0.007 to 2.93 lb/hr. The recoveries ranged from 44 to 161 percent. The average recovery was 98.7 percent with a standard deviation of 17 percent. The 95 percent confidence interval for the average recovery was 94.5 to 102.9 percent.

5.5.1.4 Repeatability of Individual Source Sampling

Repeated sampling of leaking sources was done to determine the variability of the measured leak rate. This variability is due to sampling procedures, sampling teams, process (leak) changes, and variations in the actual leak rate. Approximately 16 percent of the sampled sources were resampled at least one time.

Table 5-37 summarizes the statistical analysis of the repeat QC samples. The variability for drains is significantly higher than the other sources while the variability for relief valves is significantly less. The other sources have a standard deviation averaging about 40 percent or a 95 percent confidence limit based on a single test of ± 80 percent.

This standard deviation of 40 percent is composed of variation due to analysis, sampling train components, sampling team effect, and variability in the actual leak rate. The standard deviation for the THC analysis was

TABLE 5-37. SUMMARY OF BAGGABLE LEAK RATE QUALITY CONTROL SAMPLE

Source Type	Number Of Sources With QC	Total QC Samples	Average % Difference[1]	Standard Deviation of Sampling Analysis[2]	95% Reproducibility of Sampling/Analysis[3]	**90% Confidence Interval about a Sample Test Result**[4]
Valves	65	137	37.8	36.6	101.4%	± 71.7%
Pump Seals	62	133	44.7	41.9	116.2%	± 82.2%
Compressor Seals	40	66	39.5	38.1	105.6%	± 74.4%
Flanges	7	12	40.0	39.1	108.2%	± 76.6%
Relief Valves	16	30	18.5	19.5	54.0%	± 38.2%
Drains	14	33	71.1	59.1	163.7%	±115.8%
Overall	204	411	41.9	40.7	112.8%	± 79.8%

---

[1] Average % difference - average of pooled percent differences for each source with QC sample.

Where: % diff = [original - QC leak]/(average of original and QC leak).

[2] Standard deviation of sampling/analysis - estimated standard deviation of the sampling and analyses procedures for non-methane hydrocarbons. Estimated from the pool individual percent differences for each QC sample.

[3] 95% reproducibility of sampling/analysis - quantity that will be exceeded only about 5% of the time by the difference of two test results on a given source under similar process conditions. The quantity is equal to 2.77 x standard deviation.

[4] 90% confidence interval - When taken about a single test result, 95% of these intervals would be expected to include the "actual" leak rate (without bias considerations); the quantity is equal to 1.96 x standard deviation.

about 2.4 percent, and the standard deviation for sampling and analysis of standard gases was about 17 percent. No significant differences between sampling teams or sampling carts were found, therefore a significant portion of the variability in the measured leak rates is apparently due to real variations in the leak rate.

5.5.2 Quality Control for Hydrocarbon Screening Devices

The Bacharach TLV Sniffer was the principal device used for screening baggable sources in this study. The Century Model OVA-108 was also used for some screening activities. Each was calibrated on a daily schedule. Two concentrations of standard gases were used. Daily calibration at two concentration levels with standard gases gave consistent, unbiased readings.

The repeatability of the screening procedure (including variability of the leak rate) was investigated by performing repeated screenings on the same source by the same operators. The percent difference between duplicate readings were less than 75 percent with the TLV Sniffer and below 40 percent for the OVA-108.

5.5.3 Quality Control for Nonbaggable Sources

Quality control for nonbaggable sources (cooling towers, wastewater systems, and process stacks) involved an evaluation of the accuracy and repeatability of all analytical procedures. Sampling procedures usually do not lend themselves to accuracy evaluations although day-to-day variations give an indication of sampling repeatability.

5.5.3.1 Cooling Towers

The total organic carbon (TOC) content of cooling tower water was determined with a Dohrmann DC 52D TOC analyzer. However, the average differences for 48 comparisons of the inlet and outlet cooling water gave a standard deviation of 4.2 ppm for the analytical method. This deviation is greater than desired, and a purge-and-trap method was developed to obtain better accuracy.

An evaluation of the purge method showed that an average of 78 to 93 percent of volatile organics in standard mixtures was recovered. These standard mixtures contained less than 10 ppm volatile organics. The purge method was preferentially used to estimate losses of hydrocarbons from cooling towers.

5.5.3.2 Wastewater Systems

The purge and trap method was used to estimate losses of hydrocarbon from water passing through the wastewater treatment system. Volatile organic content of inlet and outlet oil layer samples was determined by gravimetric means. Standard mixtures of volatile hydrocarbons in a base oil were prepared. The average percent recovery of volatile hydrocarbons from these standards was 98.3 percent. The 95 percent confidence interval for the average recovery is 98.3 ± 3.5 percent.

5.5.3.3. Process Stack Emissions

The major emphasis on quality control for stack samples was on strict calibration of metering and temperature control devices, leak testing, and laboratory standard analysis.

Upon arrival at each refinery site and before setting up on a stack, all equipment was examined, set up, and the operation of all thermometers/thermocouples, pumps, and flow meters was checked. All measurement devices were calibrated. All fittings and equipment were checked for leaks both on the ground and when set up on the stack.

Quality control procedures during the analyses of the stack samples were primarily analyses of standards. Blind standards were analyzed for aldehydes, sulfur gases, and NO_x.

The percent differences for the 28 aldehyde standard analyses averaged 0.9 percent with a standard deviation of 5.2 percent. The variability appears greater at the lower concentration levels (about ± 12 percent) than for the higher concentration standards (about ± 6 percent). The aldehyde analysis procedure is concluded to be unbiased with a precision averaging about ± 10 percent.

The percent differences for the 18 sulfur analyses averaged 0.5 percent with a standard deviation of 14.6 percent. Only two standards above 100 ppm were tested. The percent differences ranged from - 39 percent to + 20 percent, but only three of the 18 analyses were low. The overall accuracy of the method for concentrations below 100 ppm is about ± 30 percent.

The three standard analyses for NO_x ranged from 21 percent to 73 percent low, indicating potential inaccuracies in the method.

5.6 Survey Information

There are many factors in a refinery which might contribute directly to the fugitive emission load or indirectly affect the overall emission level. However, they do not lend themselves to direct sampling. Among these factors are maintenance practices, laboratory techniques, unit shutdown procedures, blind changing procedures and blending operations. In order to evaluate these items, a general survey form for each of them was submitted to the refiner. The results are summarized below.

5.6.1 Maintenance Practices

Generally speaking, the refineries used combinations of in-house and contract maintenance personnel. The in-house maintenance people did much of the routine maintenance, and supplemental contract labor was used during turnarounds and larger maintenance projects.

Some form of preventive maintenance program was in force at five of six refineries. In one refinery an inspection of each unit is performed once a year. Piping, furnace tubes, etc. are replaced if it is felt that they might fail during the following year. Pumps, valves, flanges, etc. are inspected and adjusted/replaced only when a problem is reported.

At another refinery, however, a preventive maintenance program is practiced on instrumentation, electric motors and pumps. This includes a prescribed maintenance schedule for each piece of equipment. The packing and seals of pumps, valves, etc. are routinely inspected by operating personnel. Some minor adjustments may be made when the need is observed. More extensive work is done by maintenance personnel.

In five of the six refineries, equipment files are kept on pumps and compressors. Seal failures and packing leaks are recorded. However, valve maintenance records were kept at only one refinery included in this summary report.

Three of the six refineries reported that 17 percent, 18 percent and 20 percent of the operating budget is devoted to maintenance. One reported that 44 percent of its manpower was devoted to maintenance.

Significant differences in emission rates were not found among the refineries. This would indicate that the variations in maintenance programs found do not affect the emissions rates.

5.6.2 Process Unit Turnaround Procedures

Most normal maintenance in a refinery can be performed while running, but some major items require that the unit be shut down and opened. The entire unit must be purged of all hydrocarbons and tested to insure that it is "gas free." This large scale overhaul of a processing unit is called a "turnaround."

The following purging procedure is typical of industry practice. The unit is shut down and process gases are vented to a vapor recovery system, if available, or to the flare. Then steam is charged to the unit to strip out the remaining hydrocarbons. Most of this steam is vented to a closed blowdown system which will remove condensed water and route the gases to the flare. A few "high-point" vents are opened to the atmosphere during the latter stages of steaming out. The amount of hydrocarbons lost at this point is not known. However, the concentration of hydrocarbon in the unit should be low by that time. At that point, the steam flow is stopped and the unit is cooled, thus condensing the steam. The condensate is drained off. Then the vessel manways are opened and the interiors are gas tested. This procedure is thorough and effective, and its overall impact on fugitive emissions is negligible, especially in light of the infrequent nature of its occurrence.

The frequency of shutdowns for various units at one refinery is presented in Table 5-39.

5.6.3 Blind Changing

Only when handling very expensive and exotic materials, such as some lube oil stocks, would the use of blinds be warranted as a means of controlling direction of flow to prevent any cross-contamination. The refineries reported that they do not routinely change any significant number

TABLE 5-38. SHUTDOWN FREQUENCY

	Times Down in Last 12 Months	Scheduled Period Between Turnarounds
Crude Unit	1	1 year
Crude Unit	1	1 year
Catalytic Cracker	1	1 year
Fuel Reformer	0	1 year
Naphtha HDS	0	3 years
Alkylation	1	1 year
Aromatics Reformer	2	1 year
Aromatics Extraction	1	3 years

of blinds. Most blind changing takes place during the startup or shutdown of a unit, and at these times, the unit has generally been purged of hydrocarbons.

5.6.4 Sampling Procedures

Quality control sampling of light ends and volatile hydrocarbons in refineries has the potential for adding to the overall fugitive emission rate. General surveys were made of sampling, flushing and sample waste disposal procedures.

At one large refinery, laboratory personnel were observed while drawing routine liquid samples in the field. Line flushings were routed to a covered oily water drain system with a maximum of 18 inches free fall and minimum exposed retention time (i.e., less than two minutes). Readings were taken with the J. W. Bacharach "TLV Sniffer" at the drain entrance immediately before and after sampling. No significant difference in readings was discernible, and the absolute parts per million readings were below the selected sampling limit of 200 ppm. These procedures were typical of those performed at visited refineries. However, hydrocarbon screening during sample collection was not done at any other refinery.

The overall sample load at one large refinery was approximately 200 samples per day. Of these, about 40 percent were gas samples for chromatographic analysis, about 24 percent were volatile liquids (naphtha or lighter), and about 36 percent were nonvolatile liquids. Sample wastes were emptied into one of two slop oil collection systems, one for naphtha and one for heavier materials.

Daily sample loads of 50 to 200 samples per day were reported by four refineries.

PART B

REFINERY TECHNOLOGY REVIEW AND ENVIRONMENTAL ASSESSMENT

The results of the field measurement program were combined with data from other sources (literature, government agencies, vendors, etc.) to develop refinery control technology reviews/evaluations, refinery technology characterizations, and an environmental assessment of refineries. Section 6 describes potentially hazardous compounds which were found in selected refinery streams or which might be present in refinery emissions. Refinery process technology is characterized and control technology is reviewed in Section 7. An environmental assessment of petroleum refineries is contained in Section 8.

6.0 POTENTIALLY HAZARDOUS SUBSTANCES

The objective of this section is to present an overview of potentially hazardous substances which are found in refinery feed, intermediate, product, and waste streams. Since the potential for fugitive emissions exists for a wide variety of process equipment, all materials utilized in refining operations can be emitted to the atmosphere.

The term hazardous is used here to describe a compound which has shown the potential to cause adverse human health effects. The use of the term hazardous does not necessarily indicate that the chemical compound has been designated as hazardous, in a regulatory sense, by EPA. A few compounds (e.g., benzene) do fall within this legal definition of "hazardous". For these reasons, the term "potentially hazardous" is used in many instances to indicate that while the substance has the potential for causing adverse health impact, it may not be classified by EPA as hazardous, in a legal sense.

The origin of potentially hazardous substances is discussed in Section 6.1. Included are substances or classes of substances which enter the refinery as raw materials. Raw materials include the crude oil as well as numerous other chemicals required for processing. Also included in this section are substances which are formed or concentrated within refinery processes.

Section 6.2 contains a discussion of potentially hazardous substances leaving the refinery as constituents of the product streams or of solid and liquid waste streams. Also included in this section is information on the destruction of certain substances during processing.

Section 6.3 contains information on atmospheric emissions of potentially hazardous substances. Emissions from both point sources and fugitive sources are included. This section concludes with a discussion of factors which affect atmospheric emissions of potentially hazardous substances. These factors include the type of refining, the processing scheme, and the properties of the incoming crude oil.

6.1 Origin of Potentially Hazardous Substances

Many hazardous substances enter the refinery with the raw materials. Others are produced within various process units. Particular compounds or groups of compounds which enter via the above mechanisms are discussed below.

6.1.1 Potentially Hazardous Substances in Refinery Raw Materials

Many of the potentially hazardous substances found within petroleum refineries enter the refinery as constituents of crude oil. Classes of potentially hazardous materials include hydrocarbons, sulfur compounds, nitrogen compounds, and trace elements.

Hydrocarbons--A list of potentially hazardous hydrocarbons which have been identified in crude oil is given in Table 6-1. The compounds included in the table have been assigned either a threshold limit value (TLV) by the American Conference of Governmental Industrial Hygienists or a rating of 2 or 3 (capable of causing permanent damage to humans) by Irving Sax in Dangerous Properties of Industrial Materials, 1975 edition.[26]

A complete listing of all potentially hazardous substances of crude oil would be nearly impossible since there can be more than 3,000 compounds in any one crude.[27]

One group of hydrocarbons, commonly called polynuclear aromatics (PNA's), has received considerable attention due to their hazardous nature. These compounds are composed of fused aromatic rings and

TABLE 6-1. POTENTIALLY HAZARDOUS[a] HYDROCARBONS IN CRUDE OIL

Compound	Concentration[b]
Methane	T
Ethane	T
Propane	m
Methylpropane	T
Butane	m → M
Methylbutane	m
n-Pentane	m
2,2-Dimethylpropane	T → m
n-Hexane	m
2-Methylpentane	m → M
3-Methylpentane	m
2,2-Dimethylbutane	m
2,3-Dimethylbutane	m
n-Heptane	m-M
2,3-Dimethylpentane	m
2,4-Dimethylpentane	m
n-Octane	m
2-Methylheptane	m
2,3-Dimethylhexane	m
2,3-Dimethylhexane	m
2,3,4-Trimethylpentane	T
n-Dodecane	T → m
Cyclopentane	m
Cyclohexane	m
Methylcyclohexane	m → M
Cycloheptane	m
Benzene	T → m
Toluene	T → m
Ethylbenzene	T → m
Dimethylbenzene (Xylene)	T → m
n-Propylbenzene	m
Isopropylbenzene (Cumene)	m
1,2,3-Trimethylbenzene	m
1,3,4-Trimethylbenzene	m
1,3,5-Trimethylbenzene	m
Isobutylbenzene	m
sec-Butylbenzene	m
tert-Butylbenzene	m
1-Methyl-5-Isopropylbenzene	m
1,2-Diethylbenzene	m
1,3-Diethylbenzene	m

(Continued)

TABLE 6-1. Continued

Compound	Concentration[b]
1,4-Diethylbenzene	m
1-Methyl-4-tert-butylbenzene	T
1-Methylnaphthalene	T
2-Methylnaphthalene	M
Pyrene	T
Coronene	T
Benzo(a,e)pyrene	T
1,2,3,4-Tetrahydronaphthalene	T
Biphenyl	T
Acenaphthene	T
Benzofluorenes	T
Phenanthrene	T
Benzophenanthrene	T
Naphthenophenanthrenes	T
Dinaphthenophenanthrenes	T
Trinaphthenophenanthrenes	T
Tetranaphthenophenanthrenes	T
Pentanaphthenophenanthrenes	T
Fluoranthrenes	T
Perylene	T
Phenyleneperylene	T
Dibenzoperylene	T
Chrysene	T
Benzo(g)chrysene	T
3-Methylchrysene	T
Naphthenochrysenes	T
Anthracene	T
Benzanthracene	T

Sources: References 28,29,30,31,32,33,34,35,36.

[a] The compounds included in this list have either been assigned a Threshold Limit Value (TLV) by the American Conference of Governmental Industrial Hygienists or assigned a rating of 2 or 3 (capable of causing permanent damage) by Irving Sax in Dangerous Properties of Industrial Materials, 1975 edition.[26]

[b] Key to concentrations:
T = trace: <100 ppm
m = minor: 100 ppm to 2.99%
M = major: $\geq$3.0%

are found in crude oils at levels of up to 0.1 percent.[37] Several of these materials are known carcinogens.

Sulfur Compounds--The sulfur content of crude oil can vary from 0.06 to 8.0 weight percent.[38] Sulfur is incorporated into the structure of a variety of hydrocarbons and tends to concentrate in compounds of higher molecular weight.

Potentially hazardous sulfur compounds in crude oil include trace quantities of 48 thiols, almost 200 sulfides, and a number of sulfites, sulfonates, and sulfones. In lower boiling point fractions (up to 400°F), mercaptans (thiols) appear to predominate. Cyclic mercaptans appear in the kerosene range; thio-ethers and cyclic sulfides in the naphthenes. In higher boiling fractions, there is a tendency toward sulfur substitution in saturated rings.

Nitrogen Compounds--The nitrogen content of most crude oils is less than 1 percent.[38] Approximately one-fourth to one-third of this nitrogen is contained in basic compounds including alkyl-substituted quinolines and pyridines. All of these alkyl quinolines and some of the pyridines have been designated potentially hazardous by the criteria in Table 6-1. Other hazardous nitrogen compounds in crude oil include indole and the carbazoles.

Oxygen Compounds--Crude oil generally contains less than 2 percent oxygen. The oxygen compounds designated as potentially hazardous by the criteria in Table 6-1 include the lower molecular weight carboxylic acids and alkyl ketones, and some cyclic ketones and phenols.

Trace Metals--Trace quantities of a number of metals have been found in crude oil. Twenty-eight metals, most of which are considered potentially hazardous, are listed in Table 6-2. Of the metals listed, vanadium, nickel, and iron are usually present in the greatest quantities.

TABLE 6-2. TRACE METALS FOUND BY SPECTROGRAPHIC ANALYSIS OF ASH FROM CRUDE OIL

Ag	Ba	Ca	K	Mo	Pb	V
Al	Ce	Cu	La	Na	Sn	Zr
As	Co	Fe	Mg	Nd	Sr	Zn
B	Cr	Ga	Mn	Ni	Tl	U

Source: Reference 39.

In addition to crude oil, a variety of other raw materials enters the refinery. These materials, many of which are considered potentially hazardous, are used as treating agents, solvents, catalysts or additives.

Catalysts--Both solid and liquid catalysts are used in a wide range of petroleum processing operations. The hazardous nature of liquid catalysts such as hydrofluoric, sulfuric, and hydrochloric acids is well-known. Many of the solid catalysts contain metals listed as hazardous in Table 6-2.

Catalyst fines are emitted to the atmosphere during catalyst regeneration. Most catalysts are regenerated only a few times a year; therefore, the escaping catalyst fines are considered insignificant. Fluid catalytic cracking catalysts, on the other hand, are regenerated continuously. In this case, particle collection devices are used extensively to control the emissions, both for environmental protection and for economic reasons. Table 6-3 lists some of the commonly used catalysts and the processes in which they are used.

TABLE 6-3. PRINCIPAL APPLICATIONS OF CATALYST MATERIALS[a]

	Processing Application					
	Cracking	Reforming	Hydrotreating	Isomerization	Alkylation	Polymerization
Alumina	X	X	X			
Aluminum chloride				X	X	
Antimony trichloride				X		
Bauxite	X			X		
Bentonite clay	X					
Clay	X					
Cobalt-molybdena			X			
Cobalt molybdate		X	X	X		
Cobalt oxide		X				
Copper	X					
Copper pyrophosphate						X
Hydrochloric acid				X	X	
Hydrofluoric acid					X	
Iron oxide	X					
Kaolin clay	X					
Magnesia	X					
Molybdena		X				
Molybdenum		X				
Nickel sulfide			X			
Phosphoric acid						X
Platinum		X	X			
Potassium	X					
Rhenium		X				
Silica-alumina	X	X	X	X		
Sulfuric acid					X	
Tungsten nickel sulfide			X			

[a] Many catalyst materials are also used for other purposes in a refinery.

Source: Reference 40.

Gasoline Additives--Gasoline is the primary product in many refineries. Additives are introduced to improve the burning characteristics and other qualities of the gasoline. These additives include:

- Antiknock compounds such as tetraethyl lead or similar alkyl-lead compounds.
- Metal deactivators.
- Anti-corrosion additives.
- Antistall additives including light alcohols, polyalkylene glycols, and alkyl phosphates or amines.
- Antipreignition agents containing phosphorus compounds.
- Lubricants.

Many of these materials are potentially hazardous and some can form hazardous combustion products.

Other chemicals--Numerous other chemicals are utilized during the refining process. And, many are considered hazardous. Some of the major chemicals used in refining are listed with their principle uses in Table 6-4.

6.1.2 Potentially Hazardous Materials Produced in Refining Processes

Many of the potentially hazardous materials found in refinery process streams are produced within the process units rather than entering with various raw materials. Alternatively, certain other processes serve to concentrate hazardous materials, either as product or intermediate

TABLE 6-4. MAJOR CHEMICALS USED IN REFINING AND THEIR PRINCIPAL USES

Chemical	Uses
Acetic Acid	Break up emulsions Increase treating of sulfuric acid Reduce sulfur content Extract polymers from cracked distillates Separate waxes
Acetone	Regenerate clays Isolate benzene in azeotropic distillation Solvent in determining oil content of waxes
Aluminum Chloride	Cracking, alkylation, and isomerization catalyst
Aluminum Oxide (Bauxite)	Cracking catalyst
Aluminum Naphthenates	Detergent additive for lubricating oils
Aluminum Phenates	
Aluminum Soaps	
Aluminum Stearate	
Barium Hydroxide	Treat spent caustic solutions Neutralize acid-treated oils Precipitate naphthenic acids Prevent foaming before caustic soda treating for mercaptan removal Remove inorganic salts from furfural before refining
Barium Salts	Oxidation inhibitors, detergent additives in lube oils

(Continued)

TABLE 6-4. Continued

Chemical	Uses
Benzene	Solvent extraction to improve viscosity index of lube oils and remove waxes
Bone Char	Decolorize oil
Cadmium-Ammonium Chloride	Distillate Desulfurizing
Cadmium Hydroxide	
Cadmium Chloride	
Cadmium Sulfide	
Cadmium Oleate	Oxidation inhibitor in lube oil
Cadmium Naphthenate	
Cadmium Dithiocarbamate	Detergent additive
Cadmium Sulfonate	
Calcium Oxide	Neutralize acid-treated oils Remove hydrogen sulfide and organic acids from oils
Calcium Hydroxide	
Calcium Carbonate	
Calcium Chloride	Dessicant
Calcium Hypochlorite	Oxidize sulfides and mercaptans in oils
Chlorine	Oxidize disulfides to sulfonyl halides and to remove mercaptans Regenerate Bentonite clay Regenerate sodium plumbite "doctor solution" Prepare calcium and sodium hydroxide Improve cetane number of fuels

(Continued)

TABLE 6-4. Continued

Chemical	Uses
Clays	Adsorbents to improve color, odor, and stability of waxes and lube oils Cracking catalysts
Cupric Chloride	Convert mercaptans to insoluble disulfides
Cresol	Extraction of high-viscosity-index, light-color, low-carbon-residue lubricants from residual or distillate base stock
Dichloroethyl Ether	Solvent in chlorex extraction to improve viscosity index and yields of paraffinic oils
Ethanolamines (MEA, DEA, TEA)	Removal or recovery of water, hydrogen sulfide, or carbon dioxide from gaseous streams
Ethylene Dichloride	Removing wax from lube oil
Ethylene Glycol	Selective recovery of benzene, toluene, and xylenes from petroleum stocks
Formaldehyde	Laboratory reagent and solvent
Furfural	Extraction of diesel fuels, burning oils, cracking stocks, and crude oils Removal of low-cetane materials, unstable and acidic materials, sulfur, organometallic and nitrogen compounds Extraction of aromatic, naphthene, olefinic, and unstable hydrocarbons from lube oils
Hydrogen	Hydrotreating Hydrocracking Hydroalkylation

(Continued)

TABLE 6-4. Continued

Chemical	Uses
Hydrogen Fluoride	Alkylation Catalyst
Methyl Ethyl Ketone (MEK)	Remove wax from oils
Methyl Isobutyl Ketone (MIBK)	Deoiling high-quality waxes
Natural Oils	Production of lubes and greases
Nitrobenzene	Extract carbon and sludge-forming compounds from lube oils
Phenol	Extraction of high-viscosity-index, high-color, low-carbon-residue lubricants from residual or distillate base stock Improve viscosity index, color and oxidation resistance, and to reduce carbon and sludge-forming tendencies of lube oils
Phosphorous Compounds	Polymerization catalysts
Phosphorous Pentoxide	Catalyst for air-blowing of asphalt
Potassium Hydroxide	Remove acids from petroleum
Potassium Phosphate	Remove hydrogen sulfide from gas
Propane	Solvent extractions-deasphalting, dewaxing, and decarbonizing
Sodium Carbonate (Soda Ash)	Neutralize acids in processing streams
Sodium Hydroxide (Caustic Soda)	Remove acidic substances
Sodium Hypochlorite	Sweeten gasoline

(Continued)

TABLE 6-4. Continued

Chemicals	Uses
Sodium Phenolate	Remove hydrogen sulfide from gasoline Stabilize color of gasoline
Sodium Plumbite	"Doctor sweetening" agent to convert mercaptans to disulfides
Sulfur Chlorides	Solvents
Sulfur Dioxide	Extract aromatic hydrocarbons and sulfur-bearing compounds from paraffins and naphthenes Improve viscosity index and remove waxes from lube oils
Sulfuric Acid	Remove aromatics from kerosene Remove or dissolve resinous and asphaltic materials and sulfur
Toluene	Remove waxes from lube oils
Trichloroethylene	Extract carbon- and sludge-forming constituents of lube oils and increase their viscosity index

Source: Reference 40.

streams, or as waste streams. Examples of hazardous materials production or concentration are discussed in this section.

Hydrogen Sulfide--Hydrogen sulfide is an extremely toxic gas. It is found in small quantities in crude oil and is produced in a variety of refining operations including reforming, desulfurization processes, coking, catalytic cracking, and hydrocracking.

The H_2S from these processes is usually concentrated in acid-gas absorption processes for use as sulfur plant feed. Common absorption processes utilize aqueous solutions containing an alkanolamine such as monethanolamine (MEA) or diethanolamine (DEA) as the absorbing agent.

Mono-aromatic Hydrocarbons--A variety of mono-aromatic hydrocarbons are considered potentially hazardous. The simplest component in this group, benzene, is suspected of being carcinogenic and has been officially designated by EPA as a hazardous compound. These compounds are produced and purified for use in gasoline, petrochemicals, plastics, and synthetic fibers.

A refinery's major source of aromatics is usually the catalytic reforming unit. Here, hydrocarbon molecules containing six or more carbon atoms are converted to aromatics. This type of processing is useful in increasing the octane rating of certain naphthas. Products from these processes include benzene, toluene, xylenes, and other substituted aromatics.

Aromatic hydrocarbons are found in varying concentrations in a large number of refinery streams. The results of analyses conducted during this program for aromatics in 60 refinery streams are given in Appendix B (Volume 3) of this report.

Polynuclear Aromatic Hydrocarbons--As was previously discussed, polynuclear aromatic hydrocarbons are found in abundance in coal tar and are minor constituents of crude oil. Environmental concern over these compounds centers on the carcinogenic activity of certain PNA compounds. Several, most notably benzo(a)pyrene, have been shown to induce cancer, while others are suspected carcinogens or may inhibit or accelerate the activity of benzo(a)pyrene.[41] Hazardous PNA's have been identified or are suspected to be in the following refinery streams.[42]

- Catalyst regeneration gases from fixed-bed desulfurization, hydrocracking, and sweetening processes.
- Fluid catalytic cracker regenerator off gases.
- Fluid catalytic cracker cycle oil streams.
- Fluid coking off gases.
- Asphalt blowing off gases.
- Decoking operations.
- Oil-fired heater flue gas.
- Certain brines and sour water condensates.
- Flare combustion gases.
- Heavy oil sludges, wastewater system sludges, and spent catalysts.

The above list represents potential sources of atmospheric emissions of PNA's. PNA's have also been identified in other refinery streams in samples analyzed during this program. The results of these analyses are given in Appendix B (Volume 3) of this report.

Carbon Monoxide--Carbon monoxide is formed as a result of incomplete combustion. It is found in process heater flue gas and in the off gas formed during catalyst regeneration. By far, the largest source of CO in refining operations is FCC catalyst regeneration. The flue gas contains CO in concentrations ranging from 5-10 percent. This gas is usually burned in a CO boiler to recover the energy content of the off gas.

Other Potentially Hazardous Materials--A list of potentially hazardous materials has been provided in Table 6-5. For each material, a list of processes is given in which that material has been identified or is suspected present. These processes are listed as numbers and may be identified by referring to Table 6-6.

6.2 In-Line Fate of Potentially Hazardous Substances

Potentially hazardous materials present in refining streams must eventually leave the refinery. Many of these materials leave as components of the final products. Examples of this are discussed in Section 6.2.1.

Additional hazardous materials exit as components of the numerous waste streams generated during refining. Some of these waste streams require additional treatment or careful disposal to minimize environmental danger. Potentially hazardous constituents of various waste streams are discussed in Section 6.2.2.

Other hazardous materials may be destroyed prior to leaving the refinery. This may occur as a by-product of a refining process, or as a result of specific efforts to remove the material in question. Examples

TABLE 6-5. HAZARDOUS CHEMICALS POTENTIALLY EMITTED FROM PROCESS UNITS

Chemical	Potential Emission Source Process Module Numbers
Maleic Acid	1,2,3,4,7,16,17,18,19,20,22,23,24,25,26,27,28,30
Benzoic Acid	1,2,30
Cresylic Acid	3,7,16,17,18,19,20,22,23,24,25,26,27,28,30
Acetic Acid	4,30
Formic Acid	4,30
Sulfuric Acid	27,30
Diethylamine	4,5,30
Methylethylamine	4,5,30
Aromatic Amines	18,19,26,30
Ammonia	3,5,7,16,17,18,19,20,22,23,24,25,26,27,30
Chlorides	1,2,30
Sulfates	27,30
Chromates	30
Ketones	1,2,3,7,16,17,18,19,20,22,23,24,25,26,27,30
Aldehydes	1,2,3,7,16,17,18,19,20,22,23,24,25,26,27,30,32
Formaldehyde	18,19,26
Acetaldehyde	18,19,26
Carbon Monoxide	5,9,10,12,13,16,17,18,19,20,22,24,25,26,27,32
Sulfur Oxides	5,10,13,16,17,18,19,20,22,24,25,26,27,32
Nitrogen Oxides	31,32
Pyridines	1,2,3,7,16,17,18,19,20,22,23,24,25,26,27,28,30
Pyrroles	1,2,3,7,16,17,18,19,20,22,23,24,25,26,27,28,30
Quinolines	28,30
Indoles	18,19,26,30
Furans	28,27,30
Benzene	1,2,3,7,10,13,14,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30
Toluene	1,2,3,7,10,13,14,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30
Xylene	1,2,3,7,10,13,14,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30
Phenol	1,2,7,18,19,25,26,28,30
Dimethylphenol	1,2,27
Cresols	1,2,7,18,19,25,27,28,30
Xylenols	7,18,19,25,26,27,28,30
Thiophenols	26,30
Carbazoles	1,2,28,30
Anthracenes	1,2,18,19,26,28,30
Benzo(a)pyrene	18,19,26,28,32
Pyrene	18,19,26,30
Benzo(e)pyrene	18,19,26
Perylene	18,19,26,30
Benzo(ghi)perylene	18,19
Coronene	18,19,26
Phenanthrene	18,19,26
Fluoranthrene	18,19,26
Metalloporphrins	1,2,30
Nickel Carbonyl	10,16,17,20,22,24,27
Cobalt Carbonyl	10,16,17,20,22,24,27
Tetraethyl Lead	14,21
Sulfides	3,7,15,16,17,18,19,20,22,23,24,25,26,27,28,29,30
Sulfates	30
Sulfonates	3,7,16,17,18,19,20,22,23,24,25,26,27,28,29,30
Sulfones	30
Mercaptans	1,10,15,26,30
Thiophenes	1,2,3,7,16,17,18,19,20,22,23,25,25,26,27,28,30
Hydrogen Sulfide	1,3,5,7,10,13,15,16,17,18,19,20,22,23,24,25,26,27
Methylmercaptan	3,4,7,16,17,18,19,20,22,23,24,25,26,27
Carbon Dilsulfide	4,5,10,16,17,18,19,20,22,24,27
Carbonyl Sulfide	4,5,10,13,16,17,18,19,20,22,24,27
Thiosulfide	4
Dibenzothiophene	28
Alkyl Sulfide	28
Vanadium	1,2,10,16,17,18,19,20,22,24,25,26,27,28,30,32
Nickel	1,2,10,16,17,18,19,20,22,24,25,26,27,28,30,32
Lead	1,2,32
Zinc	1,2,18,19,25,26,28,30
Cobalt	10,16,17,20,22,24,27
Molybdenum	10,16,17,20,22,24,27
Copper	18,19,25,26,28,30,28
Strontium	28
Barium	28
Sulfur Particulates	5
Catalyst Fines	9,10,12,16,17,18,19,20,22,24,27
Coke Fines	10,16,17,20,22,24,25,26,27,32
Cyanides	4,5,18,19,26,30

Source: Reference 42.

TABLE 6-6. LIST OF PROCESS UNITS FOR TABLE 6-5

1	Crude storage
2	Desalting
3	Atmospheric distillation
4	Acid gas removal
5	Sulfur recovery
6	Gas processing
7	Vacuum distillation
8	Hydrogen production
9	Polymerization
10	Naphtha HDS[a]
11	Alkylation
12	Isomerization
13	Catalytic reforming
14	Light hydrocarbon storage & blending
15	Chemical sweetening
16	Kerosene HDS
17	Gas oil HDS
18	Fluid bed catalytic cracking
19	Moving bed catalytic cracking
20	Catalytic hydrocracking
21	Middle distillate storage & blending
22	Lube oil HDS
23	Deasphalting
24	Residual oil HDS
25	Visbreaking
26	Coking
27	Lube oil processing
28	Asphalt blowing
29	Heavy hydrocarbon storage & blending
30	Wastewater treating
31	Steam production
32	Process heaters

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[a] HDS = hydrodesulfurization

illustrating the destruction of certain hazardous materials are included in Section 6.2.3.

6.2.1 Potentially Hazardous Substances Present in Refinery Products

Refinery Gases--Refinery gases consist of saturated and unsaturated hydrocarbons in the C_1 to C_5 range along with varying amounts of inert gases such as N_2, H_2O, and CO_2. Also, gases such as H_2 and H_2S may be present. These gases might have been part of the original crude, or they might be by-products of certain process units. Process units producing refinery gases include atmospheric distillation, catalytic reforming, fluid catalytic cracking, hydrocracking, hydrorefining, and coking.

Hydrogen sulfide is often a constituent of raw refinery gases. It is produced from heavier sulfur compounds during hydrotreating and hydrocracking processes and is extremely hazardous. In addition to hydrogen sulfide, many of the hydrocarbons in refinery gases are considered potentially hazardous.

Aviation Gasolines--Aviation gasolines consist of high octane hydrocarbons with a boiling range of 85 to 300°F. In general, these fuels contain a high percentage of isoparaffins and smaller percentages of naphthenes and aromatics. Although most of the components of aviation gasoline are not extremely toxic, many are considered potentially hazardous. In addition, tetraethyl lead is added to prevent knocking.

Jet Fuels--Jet fuels consist of hydrocarbons with a boiling range of 300 to 460°F. The aromatic content of these fuels is limited to reduce smoke formation during combustion.

Additives are added to the fuel to control oxidation, to chelate any copper remaining after refining, to ensure that any water dissolved in the fuel will not freeze, to inhibit corrosion, and to increase conductivity and thus reduce static electricity. Most constituents of jet fuel are considered potentially hazardous.

Automobile Gasoline--Gasoline is defined as a petroleum fuel for use in reciprocating, spark-ignition, internal combustion engines. It is a complex mixture of hydrocarbons, mostly in the C_4 to C_{12} range, which distill between 85°F and 410°F. Gasolines from different refineries may vary widely in exact composition according to the processes used at the refinery. A summary of the main components of gasoline and their sources is given in Table 6-7.

Gasoline contains a relatively high proportion of aromatics, supplied mainly by the catalytic reforming process. Gasoline also contains a variety of additives including anti-knock compounds, anti-icing additives, anti-oxidants, metal deactivators, carburetor detergents, and anti-corrosion additives.

Distillate and Residual Fuels--A variety of heavier fuels are manufactured by refineries. These include diesel fuels, heating oils, gas oils, and fuel oils. Some of these fuels contain PNA's and PNA's have also been found in their combustion products. Heavier fuel oils also contain other potentially hazardous materials, including sulfur and nitrogen compounds.

Solvents (Industrial Naphtha)-- A variety of solvents are produced by refineries. These range from pure hydrocarbons such as benzene, toluene, xylene, ethylbenzene, hexane, and cyclohexane, to blends consisting of varying proportions of paraffins, cycloparaffins, and aromatics.

Asphalt--Asphalt cement is the material remaining after the removal of light and heavy distillates from asphaltic crudes. It is

TABLE 6-7. MAIN COMPONENTS OF GASOLINE

COMPONENTS	SOURCE	BOILING RANGE, °F	REMARKS
Paraffinic			
Butane	Crude oil distillation Conversion processes	30	Widely used in proportions up to 10%.
Isopentane	Crude oil distillation Conversion processes Isomerization of n-pentane	81	Widely used as high-octane, high-volatility component.
Alkylate	Alkylation process	100-300	Used widely in aviation gasoline, but less frequently in motor gasoline.
Isomerate	Isomerization process	100-160	Relatively little used at present. Excellent antiknock properties under severe engine conditions.
Straight-run Naphtha	Crude oil distillation	90-200	Widely used low-octane component.
Hydrocrackate	Hydrocracking process	100-390	Heavy products used as feed for catalytic reforming. Contains also aromatics.
Olefinic			
Thermal Reformate	Thermal reforming	100-390	Obsolescent process.
Catalytic Naphtha	Catalytic cracking	100-390	Widely used component, particularly in premium gasoline.
Steam Cracked Naphtha	Steam cracking	100-390	By-product of chemical processes.
Polymer	Polymerization of olefins	140-390	High-octane component but not widely used.
Aromatic			
Catalytic Reformate	Catalytic reforming	100-390	Most widely used high-octane component of gasolines.

Source: Reference 38.

usually mixed with distillates in varying proportions to obtain materials for specific purposes.

Cutback asphalts contain lighter distillates such as naphthas, gasoline or kerosene. They may be medium- or rapid-curing. Emulsified asphalts are emulsions of asphalt cement with chemically treated water.

"Blown asphalt" may be produced by blowing air through a residual oil at temperatures usually ranging from 400 to 600°F.[28] Asphalt blowing operations have been identified as a source of polynuclear aromatics. Compounds detected in one study included pyrene, anthracene, and trace amounts of phenanthrene and fluoranthene.[40] Asphalt also contains heavier PNA's which apparently are not volatilized at air blowing temperatures.

6.2.2 Potentially Hazardous Materials in Refinery Waste Streams

Potentially hazardous materials in solid or liquid refinery waste may find their way into ground waters or the atmosphere if improperly disposed of. Hazardous materials in the more common refinery waste streams are discussed below.

Storage Tank Bottoms--Crude oil storage tanks contain solid sediment which accumulates on the tank bottom. This sludge is usually composed of iron rust, iron sulfides, clay, sand, water, and oil. Hazardous materials contained in the sludge include various organics and organo-metallic compounds, and heavy metals found in incoming crude oil.

Tanks containing refinery products will also accumulate sludges over a period of time. Tanks with leaded products will produce sludges containing lead residues.

Wastewater Processing Sludges--Wastewater processing sludges are produced by operations including primary separation, chemical coagulation and precipitation, air flotation, and biological treatment. Since refinery wastewaters can contain water utilized in all process units, they may contain nearly any hazardous material found in the refinery. Many of these materials are found in the sludge by-product, along with chemicals used in processing the water. Volatile hazardous materials can readily leave the wastewater system due to weathering and turbulence generated by some treating units.

Spent or Neutralized Acid Sludges--Acid sludges are produced by the sulfuric acid and the hydrofluoric acid alkylation process. In addition, sulfuric acid is used as a treating agent. Spent acid from sulfuric acid alkylation is usually regenerated off-site. Spent acid from hydrofluoric acid alkylation is usually neutralized rather than regenerated. Neutralization with lime produces an insoluble calcium fluoride sludge.[37] Spent sulfuric acid from treating operations may contain a high proportion of oil.

Spent or Neutralized Caustic Solutions--Large amounts of caustic are utilized by refineries for the neutralization of acidic materials in crude oil, the neutralization of acidic products such as those formed in catalytic cracking, and for use in chemical treatment processes. These solutions may contain sulfides, mercaptans, sulfonates, phenolates, napthenates, ammonia, and various other organic and inorganic compounds.[43]

Coke Fines--Coke fines are produced during decoking operations. The coke fines produced by attrition may become airborne particulates if allowed to dry. Additionally, heavy hydrocarbons entrained in the coke may be released during the coke cutting procedure. Often, vapors are condensed during the earlier stages of decoking to recover heavier hydrocarbons. A water quench is used to minimize particulate emissions.

The feedstock to the coking unit is usually atmospheric or vacuum resid. Heavy metals present in the feed will concentrate within the coke product.[44]

Spent Clay--Filter clays are used in removing color bodies, chemical treatment residues, and trace moisture from gasoline, kerosene, jet fuel, light fuel oil and lube oil. The spent filter clay forms a sludge or cake which contains traces of oil and heavy metals.

Spent Catalysts and Catalyst Fines--Solid catalysts are used in a number of processes. These catalysts are deactivated by contaminants within the process and must eventually be replaced. These spent catalysts can contain heavy metals plus organics absorbed from process feedstocks. In some cases, the spent catalysts are reprocessed to recover their metals content.

Catalyst fines are produced by attrition within fluid-bed catalytic cracking units. These fines contain vanadium and nickel and are emitted from the catalyst regenerator. The emission of fines from this source is reduced by passing the regenerator flue gas through a series of cyclones. Further reductions are obtained using electrostatic precipitators.

Foul or Sour Water--Distillation products are often stabilized by steam stripping. The resulting condensate can contain sulfides, ammonia, mercaptans, phenolics, organic acids, nitrogen bases, and cyanides. Foul water from the catalytic cracking unit, often high in phenolics, is occasionally used as raw desalter water. In the desalter, the phenolics are absorbed by the crude oil resulting in lower phenolic loading at the wastewater treatment plant.[45]

6.2.3 Destruction of Potentially Hazardous Compounds

Several compounds, or groups of compounds which are suspected to be hazardous are not contained in either the product or waste streams. Instead these compounds are chemically converted to less toxic materials during processing. Often, the destruction of these materials is not the primary purpose of the processing step. In other cases, units are designed for specific removal of a particular contaminant. Other hazardous compounds may be eliminated by pollution abatement equipment. Examples of the destruction of hazardous materials are described below.

Hydrogenation Processes--A variety of hydrogenation processes are utilized by refiners. In most of these processes, potentially hazardous sulfur compounds are converted to H_2S. And, the products of these processes are often low in residual sulfur. Higher severity hydroprocessing can also lead to a reduction in the nitrogen content. In this case, potentially hazardous nitrogen compounds are converted to ammonia.

Hydrogen sulfide and, under certain circumstances, ammonia can be removed in a Claus sulfur plant. Tail gas from the Claus plant contains significant quantities of sulfur compounds including H_2S, SO_2, COS, and CS_2. This tail gas is either treated further to remove sulfur compounds or flared to produce SO_2, the least toxic of these sulfur compounds.

Destruction of Potentially Hazardous Materials by Combustion--A variety of potentially hazardous materials may be destroyed by combustion. These materials include:

- Hydrocarbons (mono-aromatics, PNA's, other hazardous hydrocarbons)

- Organic chemicals

- Hazardous gases (CO, H_2S)

- Hazardous solid wastes

The most common types of combustion equipment for waste disposal include flares, CO boilers, process heaters, and incinerators.

Flares--Flare systems are common to all crude oil refineries. The use of flares, or any other combustion sources, will result in the discharge of combustion pollutants such as SO_x and NO_x. Incomplete combustion can result in carbon monoxide, unburned hydrocarbons, and smoke emissions.

Combustion is improved by injecting steam into the combustion zone. Steam improves combustion by increasing turbulence, by reacting with the fuel to form oxygenated compounds that burn readily, and by retarding full polymerization that results in heavier and more difficult to burn hydrocarbons.[46]

CO Boilers--CO Boilers are commonly used to burn CO in the catalyst regenerator gas from fluid-bed catalytic cracking units and flue gas from fluid cokers. Additionally, the CO boiler is also effective in reducing the levels of aldehydes, cyanides, and hydrocarbons, including PNA's generated during catalyst regeneration.[41]

Incineration--Incineration is a disposal technique used to minimize the volume of combustible wastes. It has been used successfully on streams such as API separator bottoms, DAF float, waste biosludge, and slop oil emulsion solids. The resulting product consists of non-combustible material which occupies only 10 to 20 percent volume of the original waste.[47] Incineration can be quite effective in destroying hazardous hydrocarbons and other organic chemicals.

6.3 Atmospheric Emissions of Potentially Hazardous Substances

This section contains information on atmospheric emissions of potentially hazardous substances. Sources of atmospheric pollutants can be divided into two groups. The first group, discussed in Section 6.3.1, consists of process emission sources (point sources). The second group of sources of atmospheric emissions are fugitive sources. In contrast to point sources, the emission rates of pollutants from individual fugitive sources are quite low. However, there are thousands of fugitive sources in refineries, and fugitive emissions constitute a large portion of the total emissions from the refinery. In addition, fugitive emissions can occur on lines containing nearly any process fluid. Hence, the potential exists for atmospheric emissions of nearly every hazardous material in the refinery. Fugitive emissions of hazardous materials are discussed in Section 6.3.2.

Section 6.3.3 concludes with a discussion of miscellaneous factors affecting emissions of potentially hazardous substances. The various factors considered include the type of refinery, the type of processing units, and the type of crude oil processed.

6.3.1 Point Sources

There are several operations within the refinery which produce a waste gas stream for discharge to the atmosphere. Most of these point sources emit potentially hazardous materials. The quantity of emissions depends on the size of the unit and the degree to which control methods have been adopted for the source.

Atmospheric emissions point sources discussed in this section include:

- FCC catalyst regenerator flue gas

- Claus sulfur plant tail gas
- Asphalt blowing emissions
- Process heater flue gas
- Flare emissions

A brief discussion of the mechanism for pollutant formation and the types of hazardous materials generated is included for each source. In addition, emission factors or estimates of the quantity of emissions generated by each source are included where possible.

FCC Catalyst Regenerator Flue Gas--Coke is deposited on cracking catalysts during processing, and it must be removed to restore catalytic activity and selectivity. This is accomplished by introducing air into the regenerator and burning the coke to CO and CO_2. In conventional operation, the conversion of CO to CO_2 is minimized to avoid high temperatures which might damage internal regenerator materials. The resulting flue gas contains from 5-10 percent CO. Many refiners utilize CO-burning waste heat boiler to recover the energy contained in the flue gas and to reduce CO emissions.

Emissions from the FCC regenerator, with and without the use of a CO boiler, are listed in Section 5. Also given in that section are the results of sampling conducted during this program. The section contains a summary of data obtained from five FCC unit CO boiler stacks. Detailed information on these sampling results is given in Appendix B (Volume 3) of this report.

Aromatic species from cracking catalyst regeneration operations were also identified during this study. These compounds are listed in Tables B5-1 through B5-8 in Appendix B (Volume 3) of this report.

Claus Sulfur Plant Tail Gas--Claus sulfur plants are unable to remove all the sulfur from the acid gas feed stream. Table 6-8 shows the typical composition of a sour gas feed, the Claus unit tail gas, and the thermally incinerated tail gas.

Asphalt Blowing Unit Tail Gas--Air blowing is used to improve the hardness and increase the melting point of asphalt. Available data indicate that uncontrolled emissions amount to 60 pounds per ton of asphalt.[7] The operating conditions are favorable for the production of extremely hazardous polynuclear aromatics. The PNA's identified in one study include pyrene, anthracene, and traces of phenanthrene and fluoranthene.[41]

Process Heater Flue Gas--Potentially hazardous compounds in the flue gas of fired heaters and boilers include various sulfur and nitrogen compounds, carbon monoxide, and unburned hydrocarbons. Sulfur emissions generally occur as SO_2 and are dependent on the amount of sulfur in the fuel. Nitrogen oxide (NO_x) emissions depend on the nitrogen content of the fuel but are also influenced by the combustion conditions. Carbon monoxide and unburned hydrocarbon emissions are usually quite low. However, improper firing condition can cause a significant increase in emissions of both carbon monoxide and hydrocarbons.

EPA emission factors for process heaters are listed in Section 7 of this report.

Flares--Flares are used as final disposal method for hydrocarbon gases and other waste gas streams. In general, emissions of carbon monoxide and hydrocarbons from flares are higher than those from process heaters of boilers. Factors which may account for less effective combustion in flares include:

TABLE 6-8. TYPICAL CLAUS TAIL GAS COMPOSITIONS[a]

Component	Sour Gas Feed, Volume %[b]	Claus Tail Gas, Volume %[b]	Thermally Incinerated Tail Gas, Volume %[b]
H_2S	89.9	0.85	0.001
SO_2	0.0	0.42	0.89
S_8 vapor	0.0	0.10 as S_1	0.00
S_8 aerosol	0.0	0.30 as S_1	0.00
COS	0.0	0.05	0.02
CS_2	0.0	0.05	0.01
CO	0.0	0.22	0.10
CO_2	4.6	2.37	1.45
O_2	0.0	0.00	7.39
N_2	0.0	61.04	71.07
H_2	0.0	1.60	0.50
H_2O	5.5	33.00	18.57
H.C.	0.0	0.00	0.00
	100.0	100.00	100.00
Temperature, °C	40	140	400
Pressure, atm.	1.45	1.1	1
Total gas volume[2]	--	3.0 x feed gas volume	5.8 x feed gas volume

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[a] Two catalytic reactors - overall efficiency of 94%.

[b] Gas volumes compared at standard conditions.

Source: Reference 48.

- Variable firing rates which make control of steam and combustion air flow rates difficult.

- Variable heat values for fuel which may also contain significant quantities of olefins or aromatics.

- Relatively low combustion temperatures with short residence times compared to process heaters and boilers.

Emission factors for smokeless flares are listed in Section 7. The emissions listed are given as pounds of pollutant per thousand barrels of refinery capacity.

6.3.2 Fugitive Sources

To quantify fugitive emissions of a particular component, the emission rate of each type of source emitting that component must be known. In addition, knowledge of the total number of each source type and the concentration of the component within the leaking process stream is also required.

During the course of this program, Radian has accumulated much of the information required for such an anlysis. Estimates of total fugitive emissions of a particular component may be estimated in a direct manner using that data. For example, the following procedure can be used to estimate the emissions of any hazardous substance from a refinery process unit. The first step consists of identifying different process streams characteristic to the unit. Then, the fugitive emission sources, developed from source counts taken during this program, are divided between the available process streams.

Finally, the component analyses can be applied to these process stream emissions. That is, total stream emissions are multiplied by the weight fraction of each component in the process stream. And, total emissions of a particular component will be the sum of emissions from all refinery streams containing that component.

Radian has performed this analysis for a number of pure components. Other components have been consolidated into groups containing compounds with similar chemical properties. The results of this analysis, given in Table 6-9, show total fugitive emissions from a large existing refinery model (see Appendix D, Volume 4) on a component basis. This procedure is discussed in detail in Appendix D (Volume 4) of this report.

6.3.3 Miscellaneous Factors Affecting Emissions of Hazardous Substances

The characteristics of the crude oil and the type of processing utilized by a refinery can have a marked effect on the quantity of various hazardous materials emitted to the atmosphere. Factors influencing emissions of hazardous substances are discussed below.

Characteristics of Crude Oil--Fugitive emissions sources include equipment located in every process unit in the refinery. Hence, it is likely that all materials contained in the crude oil feed to the refinery will be emitted to the atmosphere to some extnet.

The concentration in crude oil of several groups of potentially hazardous materials can vary widely. These groups include sulfur and nitrogen containing compounds, aromatics, and heavy metals. Sulfur and nitrogen are incorporated into the structures of a wide variety of compounds, many of which are potentially hazardous. High sulfur crudes may require substantial hydrodesulfurization to meet product specifications. This increases the quantity of hydrogen sulfide fed to the sulfur recovery unit and results in increased emissions of sulfur compounds with the tail gas.

TABLE 6-9. SUMMARY OF HYDROCARBON SPECIES EMISSIONS FROM FUGITIVE SOURCES IN A LARGE EXISTING REFINERY MODEL (SEE APPENDIX D, VOLUME 4)

Component	Source							
	V, P, C, F, D, CT*		Relief Valves		API Separators		Totals	
	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr
Benzene	7,200	2.8	23,000	0.4	700	0.4	3,900	3.6
Toluene	21,000	8.2	24,000	0.4	2,200	1.1	11,000	9.7
Ethylbenzene	5,600	2.2	4,500	0.1	590	0.3	2,800	2.6
Xylenes	31,000	12.1	26,000	0.4	2,100	1.1	15,000	13.6
Other Alkylbenzenes	42,000	16.6	35,000	0.6	7,900	4.1	23,000	21.3
Naphthalene	1,700	0.7	1,400	0.02	2,900	1.5	2,400	2.2
Anthracene	20	0.01	1	0.0	390	0.2	220	0.2
Biphenyl	230	0.1	110	0.0	1,800	0.9	1,100	1.0
Other PNA's	7,700	3.0	3,300	0.05	1,500	0.8	4,200	3.9
n-Hexane	16,000	6.3	9,700	0.2	*i***	*i*	7,100	6.5
Other Alkanes	654,000	255.9	678,000	11.3	980,000	502.4	840,000	769.6
Olefins	46,000	18.1	30,000	0.5	*i*	*i*	20,000	18.6
Cycloalkanes	135,000	52.9	82,000	1.4	*i*	*i*	59,000	54.3
Hydrogen	31,000	12.3	82,000	1.4	*i*	*i*	15,000	13.7
TOTALS		391.2		16.8		512.8		920.8

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* Fugitive emissions from valves, pumps, compressors, flanges, drains, and cooling towers.

** Components marked with "*i*" are indicated present, but no quantifiable concentration data were available.

Effect of Processing--An important finding of this program is that both the frequency and the magnitude of fugitive leaks increase with increasing volatility of material being processed. Therefore, fugitive emissions, on a per source basis, are most likely higher from refineries with substantial light ends processing or refineries producing gasoline as opposed to heating oil.

7.0 REFINERY CHARACTERIZATION AND CONTROL TECHNOLOGY

The individual refinery technologies are described in Section 7.1. Refinery control technology is discussed in Section 7.2. Existing and available control techniques are included for fugitive and process emission sources.

7.1 Refinery Technology Characterization

This section contains a brief description of each of the major refinery processes and a description of their respective emissions. Emission factors for fugitive emission sources were determined as a part of the refinery assessment program.

The estimated fugitive nonmethane hydrocarbon emissions from each source type and stream category as well as an estimate of emissions from the entire unit are included for most processes. Many of these estimates are listed as a range because of variations in the estimated sources and source distributions. In addition to the source counts and estimates developed by Radian, a second set of source counts is given for most process units. These counts were based on information contained in a study by Pacific Environmental Services (PES).[49] In this study, process flow diagrams were used to determine the number of pumps and compressors within the unit. Other sources were estimated from pump counts.

It must be emphasized that all of the source counts and stream service distributions given in this report are, at best, rough estimates. Even those values based on actual source count data should be considered rough estimates since only a small number of process units were counted. In addition, source counts for similar types of process units showed large variations. Therefore, reliable estimates for emissions source counts and distributions should be obtained for the particular process unit in question rather than using the estimates which are designed to characterize typical refinery operation.

Additional information concerning the emissions estimates is contained in Appendix B (Volume 3) and Appendices C and D (Volume 4) of this report. More detailed process descriptions are included in Appendix F (Volume 5).

7.1.1 Separations

Crude oil is separated by distillation into a variety of intermediate products which are used as feedstocks for downstream processing units. Boiling ranges of each fraction vary with the intended use for the fractions.

Higher efficiencies and lower costs are achieved if crude oil separation is accomplished in two steps: (1) fractionating the total crude stream at atmospheric pressure, then (2) fractionating under a high vacuum the high boiling bottoms fraction (topped crude) from the first fractionation. A third separation in petroleum refineries is the extraction of aromatic compounds from reformate streams. These aromatics are then used in gasoline blending or petrochemical operations.

7.1.1.1 Atmospheric Distillation

Nearly all crude oil feed must pass through a refinery's atmospheric distillation unit before it can be further processed. Atmospheric distillation separates the hydrocarbon components of the crude into fractions by distillation and steam stripping.

Process Conditions--Typical operating parameters and utility requirements for an atmospheric distillation unit with a capacity of 24,000 bbl/day are listed below:

- Pressure: Atmospheric
- Temperature: 250°F - at top of fractionator
  700°F - at bottom of fractionator
- Electricity: 4.1 kW/bbl
- Thermal Energy: 10^5 Btu/bbl
- Steam: 50 lb/bbl
- Process Water: 50 gal/bbl

Potentially Hazardous Atmospheric Emissions--Emissions from atmospheric distillation operations include process heater flue gas emissions and fugitive emissions. These emissions are summarized in Tables 7-1 and 7-2. Table 7-3 provides information on the composition of the fugitive emissions.

7.1.1.2 Vacuum Distillation

Vacuum distillation is used to fractionate topped crude from the atmospheric distillation unit into a heavy residual oil and one or more heavy gas oil streams. A vacuum distillation unit is an integral part of most refineries.

Process Conditions--Typical operating parameters and utility requirements for a vacuum distillation unit are listed below:

- Temperature: 750 to 830°F.
- Pressure: 0.4 to 0.7 psia.
- Thermal Energy: 74,900 Btu/bbl.

TABLE 7-1. TYPICAL EMISSIONS FROM ATMOSPHERIC DISTILLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of crude oil feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.4
- Residual oil		
Grade 4	7	5.0
Grade 5	10	7.1
Grade 6	10(S)+3	7.1(S)+2.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	101(S)
- Residual oil	157(S)	112(S)
Sulfur Trioxide[c]	2(S)	1.4(S)
Carbon Monoxide[d]	5	3.6
Hydrocarbons (as CH_4)[d]	1	0.71
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	16
- Residual oil[e]	$22+400(N)^2$	$16+286(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.48-1.43
Sulfur Oxides (as SO_2)[f]	0.6	0.057
Carbon Monoxide	17	1.6
Hydrocarbons (as CH_4)	3	0.29
Nitrogen Oxides (as NO_2)	120-230	11.4-21.9

[a] Source: Reference 7.

[b] Based on a heat input of 1.0×10^5 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-2. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL ATMOSPHERIC DISTILLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d,e]		
Valves	Gas/Vapor	89	263 - 270	0.059	5.25 - 15.9
	Light Liquid (VP > 0.1 psia @ 100°F)	281	1663 - 1727	0.024	6.74 - 41.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	523	704 - 703	0.0005	0.262 - 0.352
	Hydrogen Service	0	0	0.018	0.0
	Total	893[a]	2630 - 2700[c]		12.3 - 57.7
Open-End (Sample) Valves	All	-	56 - 57[b]	0.005	0.280 - 0.285
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	11(15)	26(36)-27(38)	0.25	3.75 - 9.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	20(28)	11(15)-11(15)	0.046	0.690 - 1.29
	Total	31(43)[a]	37(52)-38(53)[b]		4.44 - 10.8
Drains	All	69[a]	-	0.070	4.83
Flanges & Fittings	All	3997[a]	8695 - 8930[c]	0.00056	2.24 - 5.00
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	1(2)	0	1.4	0.0 - 2.80
	Hydrogen	0	0	0.11	0.0
	Total	1(2)[a]	0		0.0 - 2.80
					25.2 - 82.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

[e] This PES estimate includes vacuum distillation as part of the crude distillation unit. Radian estimates for emissions from vacuum distillation are listed in Section 7.1.1.2 and may be added to the Radian estimates for atmospheric distillation for comparison to the PES estimates.

TABLE 7-3. ESTIMATED COMPOSITION OF NONMETHANE HYDROCARBON FUGITIVE EMISSIONS FROM A CRUDE DISTILLATION UNIT[a]

	Stream				
	Crude Oil	Straight run naphtha	Middle distillate	Atmospheric gas oil	Totals
Estimated percentage of emissions attributed to each stream - %	74	24	1	1	100%
Weighted contribution of each component to unit emissions - ppmw [b]					
Benzene	46	59	0	0	105
Toluene	522	617	0	0	1139
Ethylbenzene	169	208	0	0	377
Xylenes	676	382	1	0	1059
Other Alkylbenzenes	2871	3904	8	1	6784
Naphthalene	660	344	1	0	1005
Anthracene	108	1	1	0	110
Biphenyl	246	147	0	0	393
Other Polynuclear Aromatics	6051	3528	56	2	9637
n-Hexane	13820	9167	0	0	22987
Other Alkanes	673680	117660	8627	9724	809691
Olefins	0	0	0	0	0
Cyclo Alkanes	44770	99503	1024	512	145809
					999096

[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

- Electricity: 0.10 to 0.20 kW/bbl.

- Steam: 8 lb/bbl.

Atmospheric Emissions--Emissions from vacuum distillation units include emissions from steam ejectors and barometric condensers, process heater flue gas emissions, and fugitive emissions.

The size and number of ejectors and condensers used are determined by the vacuum needed and the vapor load. To maintain a fractionator pressure of no more than 0.4 psia, three ejector stages are usually required. Process hydrocarbon emissions from steam ejectors have been estimated at 50 lb/10^3 bbl charge. If barometric condensers are used, emissions may be as much as 1,060 lb/10^3 bbl charge. Noncondensable hydrocarbon vapors removed by the ejector system are released to the atmosphere unless combusted in a furnace firebox or other combustion device. Fugitive emissions and emissions from process heaters are summarized in Tables 7-4 and 7-5.

7.1.1.3 Aromatics Extraction

Aromatics are extracted from reformate streams by a liquid/liquid solvent extraction process. There are a number of proprietary commercial extraction processes. The Sulfolane and Udex processes account for the majority of commercial installations for aromatics extraction: each is in use in more than 50 refineries throughout the world. The Tetra process is installed in more than 35 refineries. Sulfolane, originally developed by Royal Dutch/Shell, is licensed by the UOP Process Division of UOP, Inc., as Udex. The Tetra licensor is Union Carbide Corporation. Most of the remaining commercial installations are processes licensed by Howe-Baker Engineers (Aromex), Snamprogetti S.p.A. (Formex), and the Institute Francais due Petrole (IFP).

TABLE 7-4. TYPICAL EMISSIONS FROM VACUUM DISTILLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	**Total Emissions**[b] ($lb/10^3$ bbl of crude oil feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.4
- Residual oil		
Grade 4	7	5.0
Grade 5	10	7.1
Grade 6	10(S)+3	7.1(S)+2.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	101(S)
- Residual oil	157(S)	112(S)
Sulfur Trioxide[c]	2(S)	1.4(S)
Carbon Monoxide[d]	5	3.6
Hydrocarbons (as CH_4)[d]	1	0.71
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	16
- Residual oil[e]	$22+400(N)^2$	$16+286(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.48-1.43
Sulfur Oxides (as SO_2)[f]	0.6	0.057
Carbon Monoxide	17	1.6
Hydrocarbons (as CH_4)	3	0.29
Nitrogen Oxides (as NO_2)	120-230	11.4-21.9

[a] Source: Reference 7.

[b] Based on a heat input of 1.0×10^5 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE 7-5. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL VACUUM DISTILLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	50	71	0.059	2.95 - 4.19
	Light Liquid (VP > 0.1 psia @ 100°F)	45	142	0.024	1.08 - 3.41
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	405	497	0.0005	0.203- 0.249
	Hydrogen Service	0	0	0.018	0.0
	Total	500[b]	710[b]		4.23 - 7.85
Open-End (Sample) Valves	All	-	14[a]	0.005	0.070
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(2)	2(3)	0.25	0.50 - 0.75
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	14(20)	7(10)	0.046	0.46 - 0.92
	Total	16(22)[b]	9(13)[a]		0.96 - 1.67
Drains	All	42[b]	-	0.070	2.94
Flanges & Fittings	All	1785[b]	2350[b]	0.00056	1.00 - 1.32
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0	1.4	0.0
	Hydrogen	0	0	0.11	0.0
	Total	0	0		0.0
					10.3 - 15.0

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 49,

Tetraethylene glycol, mixtures of several glycols, dimethylsulfoxide, formul-morpholine, and tetrahydrothiophene-dioxide are some of the solvents used.

Process Conditions--Typical operating parameters for the most widely used processes are given in Table 7-6.

Atmospheric Emissions--Since aromatics extraction is a closed process, the only significant emissions are fugitive hydrocarbon emissions. These emissions are summarized in Tables 7-7 and 7-8.

7.1.2 Thermal Operations

Thermal operations are noncatalytic processes used to convert large hydrocarbon molecules into smaller molecules at high temperatures. These processes convert low value stocks such as heavy gas oil into lighter, more valuable products. The thermal operations currently used by U.S. refineries include delayed coking, fluid coking, visbreaking, and thermal cracking.

7.1.2.1 Visbreaking

Visbreaking (viscosity breaking) is a mild thermal cracking operation used to reduce the viscosity of materials such as atmospheric or vacuum residuals and pitch. This procedure reduces the amount of valuable light heating oil which must be blended with the residuum to produce a fuel oil of acceptable viscosity.

Process Conditions--Typical operating parameters and utility requirements for a visbreaking operation are given below.[38,50]

TABLE 7-6. OPERATING PARAMETERS AND UTILITY REQUIREMENTS FOR THREE AROMATICS EXTRACTION PROCESSES

Condition	Process		
	Udex	Sulfolane	Tetra
Stripping Steam Ratio, wt/wt	0.6	0.13	---
Stripper Bottom Temperature, °F	290	375	---
Extractor Top Temperature, °F	290	212	---
Extractor Pressure, psig	110	15	---
Feed Temperature, °F	240	240	---
Utilities, per barrel of feed			
Steam, lb	400	2.5	125
Fuel, 10^3 btu	---	190	---
Cooling Water, gal.	1,200	530	650
Electricity, kWh	1.3	0.8	0.3

TABLE 7-7. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL AROMATIC EXTRACTION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	60	206	0.059	3.54 - 12.2
	Light Liquid (VP > 0.1 psia @ 100°F)	486	1370	0.024	11.7 - 32.9
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	54	483	0.0005	0.027 - 0.242
	Hydrogen Service	0	0	0.018	0.0
	Total	600[b]	2059[b]		15.3 - 45.3
Open-End (Sample) Valves	All	-	29[a]	0.005	0.145
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	16(23)	17(24)	0.25	5.75 - 6.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	2(3)	6(8)	0.046	0.138 - 0.368
	Total	18(25)[b]	23(32)[a]		5.89 - 6.37
Drains	All		-	0.070	3.29
Flanges & Fittings	All	2142[b]	6815[b]	0.00056	1.20 - 3.82
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0	1.4	0.0
	Hydrogen	0	0	0.11	0.0
	Total	0	0		0.0
					27.0 - 59.6

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 49,

TABLE 7-8. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM AN AROMATICS EXTRACTION UNIT[a]

	Stream				
	Reformate	Solvent	Aromatic Extract	Raffinate	Totals
Estimated percentage of emissions attributed to each stream - %	12	0	44	44	100%
Weighted contribution of each component to unit emissions - ppmw[b]					
Benzene	648	0	7850	22	8520
Toluene	9324	0	112948	330	122602
Ethylbenzene	4020	0	48695	132	52847
Xylenes	20508	0	248420	660	269588
Other Alkylbenzenes	38928	0	21120	1012	61060
Naphthalene	858	0	44	22	954
Anthracene	0	0	0	0	0
Biphenyl	0	0	0	0	0
Other Polynuclear Aromatics	84	0	44	22	150
n-Hexane	2880	0	44	27720	30644
Other Alkanes	42720	0	836	410080	453637
Olefins	0	0	0	0	0
Cyclo Alkanes	0	0	0	0	0
					1000000

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[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

- Temperature: 850 to 950°F.

- Pressure: 50 to 300 psig.

- Electricity: 0.47 kWh/bbl.

- Steam (300 psig): 8.7 lb/bbl.

- Fuel: 88×10^3 Btu/bbl.

Atmospheric Emissions--Emissions from visbreaking operations include process heater flue gas and fugitive emissions. A typical visbreaking unit will have one heater. Emissions from this heater are summarized in Table 7-9. Fugitive emissions are summarized in Table 7-10.

7.1.2.2 Delayed Coking

Delayed coking is a semicontinuous process in which the heated charge (heavy gas oil or residuum) is transferred to large coking drums. The coking drums provide sufficient residence time for the cracking reactions to proceed to completion. During the reaction, coke is produced and deposited within the coke drum. Delayed coking is likely to remain an important refining process since it simultaneously converts low-value materials to lighter, more valuable products while producing coke as a valuable by-product.

In many cases, the coker is mounted over a railroad track so that the coke can be discharged directly into railroad cars. The coke is retained in the cars while water and coke fines drain off and flow to a sump. Alternatively, the coke can be directed to a concrete apron or pit.

Process Conditions--Temperature and pressure influence the rate of cracking and coking reactions. At higher heater outlet temperatures

TABLE 7-9. TYPICAL EMISSIONS FROM VISBREAKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	**Total Emissions**[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.3
- Residual oil		
Grade 4	7	4.5
Grade 5	10	6.4
Grade 6	10(S)+3	6.4(S)+1.9
Sulfur Dioxide[c]		
- Distillate oil	142(S)	91.3(S)
- Residual oil	157(S)	101(S)
Sulfur Trioxide[c]	2(S)	1.3(S)
Carbon Monoxide[d]	5	3.2
Hydrocarbons (as CH_4)[d]	1	0.64
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	14
- Residual oil[e]	$22+400(N)^2$	$14+257(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.43-1.29
Sulfur Oxides (as SO_2)[f]	0.6	0.051
Carbon Monoxide	17	1.5
Hydrocarbons (as CH_4)	3	0.26
Nitrogen Oxides (as NO_2)	120-230	10.3-19.7

[a] Source: Reference 7.

[b] Based on a heat input of 9.0×10^4 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-10. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL VISBREAKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	30	0.059	1.77
	Light Liquid (VP > 0.1 psia @ 100°F)	46	0.024	1.10
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	224	0.0005	0.112
	Hydrogen Service	0	0.018	0.0
	Total	300[a]		2.98
Open-End (Sample) Valves	All	20[a]	0.005	0.100
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(2)	0.25	0.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	0.046	0.46
	Total	9(12)[a]		0.96
Drains	All	23[a]	0.070	1.61
Flanges & Fittings	All	1071[a]	0.00056	0.60
Relief Valves	All	6[a]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	1.4	0.0
	Hydrogen	0	0.11	0.0
	Total	0		0.0
				7.29

[a] Estimated

and/or increased drum pressure, the yield of gas, naphtha and coke is increased at the expense of a lower gas oil yield. Typical operating parameters for delayed coking are shown below.[38,50,51,52]

- Heater outlet temperature: 900 to 975°F.
- Coke drum pressure: 20 to 100 psig.
- Recycle ratio: 0.1 to 1.0.

Atmospheric Emissions--Emissions from delayed coking operations include emissions from decoking operations, process heater flue gas, and fugitive emissions.

The steam injected into the drum as part of the decoking operation is condensed and the remaining vapors usually flared. During the removal of the coke from the drum, particulates are released, as are hydrocarbon vapors entrained in the coke. A water quench is often used to minimize particulate emissions. This water contains sulfur components and it may be a source of objectionable odors. Emission factors for the decoking operation were not available. Process heater and fugitive emissions are summarized in Tables 7-11, 7-12, and 7-13.

7.1.2.3 Fluid Coking

Fluid coking, like delayed coking, was developed to convert residuals, tars, and resins produced during certain refining operations to lighter, more valuable liquid products and coke. Yields are similar to those from delayed coking, except that coke production is significantly lower. Also, the coke produced is usually of insufficient quality for industrial use.[38,53]

TABLE 7-11. TYPICAL EMISSIONS FROM DELAYED COKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	**Total Emissions**[b] (lb/10^3 bbl of coker feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	3.4
- Residual oil		
Grade 4	7	12
Grade 5	10	17
Grade 6	10(S) + 3	17(S) + 5.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	243(S)
- Residual oil	157(S)	269(S)
Sulfur Trioxide[c]	2(S)	3.4(S)
Carbon Monoxide[d]	5	8.6
Hydrocarbons (as CH_4)[d]	1	1.7
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	38
- Residual oil[e]	$22+400(N)^2$	$38+686(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.1-3.4
Sulfur Oxides (as SO_2)[f]	0.6	0.14
Carbon Monoxide	17	3.9
Hydrocarbons (as CH_4)	3	0.69
Nitrogen Oxides (as NO_2)	120-230	27-53

[a] Source: Reference 7.

[b] Based on a heat input of 2.4×10^5 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-12. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL DELAYED COKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	30	178	0.059	1.77 - 10.5
	Light Liquid (VP > 0.1 psia @ 100°F)	57	1308	0.024	1.37 - 31.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	213	291	0.0005	0.107 - 0.146
	Hydrogen Service	0	0	0.018	0.0
	Total	300[b]	1777[b]		3.25 - 42.0
Open-End (Sample) Valves	All	-	43[a]	0.005	0.215
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(3)	18(25)	0.25	0.750 - 6.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	4(6)	0.046	0.460 - 0.276
	Total	9(13)[b]	22(31)[a]		1.21 - 6.53
Drains	All	23[b]	-	0.070	1.61
Flanges & Fittings	All	1071[b]	5875[b]	0.00056	0.60 - 3.29
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	3(6)	1.4	0.0 - 8.4
	Hydrogen	0	0(0)	0.11	0.0
	Total	0	3(6)		0.0 - 8.4
					8.03 - 63.5

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 49.

TABLE 7-13. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A DELAYED COKING UNIT[a]

	Stream					
	Vacuum Resid	Coke	Cracked Naphtha	LPG Olefins	Fuel Gas	Totals
Estimated percentage of emissions attributed to each stream - %	0	0	57	14	29	100%
Weighted contribution of each component to unit emissions - ppmw[b]						
Benzene	0	0	1642	0	0	1642
Toluene	0	0	51175	0	0	51175
Ethylbenzene	0	0	12215	0	0	12215
Xylenes	0	0	97727	0	0	97727
Other Alkylbenzenes	0	0	138778	0	0	138778
Naphthalene	0	0	6242	0	0	6242
Anthracene	0	0	0	0	0	0
Biphenyl	0	0	0	0	0	0
Other Polynuclear Aromatics	0	0	3694	0	0	3694
n-Hexane	0	0	6743	0	0	6743
Other Alkanes	0	0	116340	56000	266800	439140
Olefins	0	0	97322	84000	17400	198722
Cyclo Alkanes	0	0	38122	0	0	38122
Hydrogen	0	0	0	0	5800	5800
						1000000

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[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

Flexicoking is a relatively recent integration of conventional fluid coking and coke gasification. The coke gas produced may be substituted for refining fuel gas or natural gas. The net coke production is 1 - 2 weight percent of the feed, as compared to 10 - 20 percent for conventional fluid coking. No commercial flexicokers have been installed in the U.S., but extensive commercial experience has been accrued abroad.[54]

Process Conditions--Fluid coking and flexicoking operating conditions are summarized in Table 7-14.

Potentially Hazardous Atmospheric Emissions--Emissions from fluid coking include burner vessel flue gas and fugitive emissions. No process heaters are needed, because heat is supplied by the coke.

Combustion of the coke produces a flue gas containing substantial quantities of carbon monoxide with lesser amounts of SO_x, NO_x, organics, and particulates. CO emission rates have been estimated at 30 pounds per barrel of feed.[55] CO boilers are used to recover the substantial energy in this gas and to reduce the concentrations of CO and other combustibles. However, high combustion temperatures may cause an increase in NO_x emissions. Both SO_x and NO_x concentrations will increase if auxiliary fuel is used.

Fugitive emissions are summarized in Table 7-15.

7.1.3 Cracking Operations

Cracking operations convert heavy petroleum fractions into lighter, more valuable products. Two processes, catalytic cracking and hydrocracking, provide a substantial portion of the cracking capacity in the United States. Although these processes are similar in that they crack heavy fractions to produce lighter products, there are considerable differences between them in both the operating principles and the pollution potential. The choice of one process over the other is usually an economic one.

TABLE 7-14. PROCESS CONDITIONS FOR FLUID COKING AND FLEXICOKING

	Fluid Coking	Flexicoking
Temperature, °F		
Reactor	950	950
Burner	1,150	1,150
Gasifier	---	1,300-1,800
Pressure, psig		
Reactor	10	10
Burner	11	11
Gasifier	---	24-45
Utilities - per barrel feed		
Electric Power, kWh	5.5	13
Fuel, MM Btu	0	0

Source: References 38,50,54,56.

TABLE 7-15. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL FLUID COKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	30	0.059	1.77
	Light Liquid (VP > 0.1 psia @ 100°F)	58	0.024	1.39
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	216	0.0005	0.108
	Hydrogen Service	0	0.018	0.0
	Total	304[a]		3.27
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(3)	0.25	0.75
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	0.046	0.46
	Total	9(13)[a]		1.21
Drains	All	28[a]	0.070	1.96
Flanges & Fittings	All	1047[a]	0.00056	0.586
Relief Valves	All	6[b]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	4(8)	1.4	11.2
	Hydrogen	0(0)	0.11	0.0
	Total	4(8)[a]		11.2
				19.4

[a] Physically Counted

[b] Estimated

7.1.3.1 Catalytic Cracking

Several types of catalytic cracking processes have been developed: fluid-bed catalytic cracking (FCC) units, and moving bed designs such as Thermofor (TCC) and Houdriflow (HCC) cracking units. With the advent of new catalysts, major design and operational changes have been incorporated in FCC unit operation. By contrast, no major changes in moving bed type units have been observed and these units are being phased out.

In a typical FCC unit the reactor contains a bed of powdered catalyst which is kept in a fluidized state by the flow of vaporized feed material and steam.

Thermofor and Houdriflow catalytic cracking units use beaded or pelleted catalysts.

Process Conditions--Typical operating conditions for a conventional FCC unit and for one with high temperature regeneration (HTR) are given in Table 7-16.

Atmospheric Emissions--Emissions from catalytic cracking units include catalyst regeneration emissions, process heater flue gas emissions, and fugitive emissions.

Many refiners use a CO-burning waste heat boiler to recover the energy contained in the flue gas from the regenerator. This boiler also significantly reduces the emission of CO and other combustible contaminants. Increased emissions of "thermal NO_x" may occur, however, along with the production of SO_x from sulfur in the auxiliary fuel. Typical emission levels for regenerator flue gas with and without a CO boiler are given in Table 7-17. This table also lists results of sampling conducted during this program. Detailed information on these sampling results is given in Appendix B (Volume 3 of this report).

TABLE 7-16. TYPICAL OPERATING CONDITIONS FOR FLUID CATALYTIC CRACKING

Reactor Temperature, °F	885 - 1,025
Regenerator Temperature, °F	
Conventional Regeneration	1,000 - 1,100
HTR	1,100 - 1,350
Coke Content of Spent Catalyst, Wt %	
Conventional Regeneration	6
HTR	5
Coke Content on Regenerated Catalyst, Wt %	
Conventional Regeneration	0.2 - 0.3
HTR	0.01 - 0.1

Source: References 57,58.

TABLE 7-17. EMISSION RATES FROM FCC REGENERATORS, BEFORE AND AFTER CO BOILER

	Emissions without CO Boiler	Emissions with CO Boiler		
Chemical Species[a]	(Reference 58)	(Reference 58)	Data from Current Program[b]	Total Emissions Based on Data from Current Program - (lb/1000 bbl feed)
SO_2, ppmv	130-3300	Up to 2700	14.4-871	8-382
SO_3, ppmv	NA[c]	NA[c]	0.65-13.5	0.5-9.0
NO_x (as NO_2), ppmv	8-394	Up to 500	94.1-453	41-193
CO, % Vol.	7.2-12.0	0-14 ppmv	0.0-1.0	0.0
CO_2, % Vol.	10.5-11.3	11.2-14.0	13.5-16.1	-
O_2, % Vol.	0.2-2.4	2.0-6.4	3.2-7.0	-
N_2, % Vol.	78.5-80.3	82.0-84.2	77-82.7	-
H_2O, % Vol.	13.9-26.3	13.4-23.9	9.2-22.7	-
Hydrocarbons, ppmv	98-1213	NA[c]	0.28-46.2	1.1-12.0
Ammonia, ppmv	0-675	NA[c]	0.0-15.4	0.06-1.65
Aldehydes, ppmv	3-130	NA[c]	0.0-19.6	0.0-4.6
Cyanides, ppmv	0.19-0.94	NA[c]	0.0-19.1	0.0-4.54
Particulates, gr/SCF	0.08-1.39	0.017-1.03	0.012-0.304	7.9-45.2
Temperature, °F	1000-1200	485-820	386-727	-

[a] All concentrations on dry basis

[b] Based on sampling of 5 stacks

[c] Not available

High temperature regeneration or combustion promotion catalysts can reduce the level of CO in the regenerator flue gas to 200 - 2,000 ppm, usually < 500 ppm.[58] Because the temperatures involved are lower than those in a CO boiler, thermal NO_x emissions are somewhat lower.[58] Fugitive emissions and emissions from process heaters are summarized in Tables 7-18, 7-19 and 7-20.

7.1.3.2 Hydrocracking

Hydrocracking is a high-temperature, high-pressure process for converting heavy feedstocks into lighter products in the presence of hydrogen and a catalyst or series of catalysts. The process is highly flexible and produces low-sulfur, low-nitrogen products. A hydrocracker may be single-stage or two stage.[38,51,59,60]

Process Conditions--The severity of the process conditions required for hydrocracking depends on the type of feedstock and the degree of cracking desired. The primary reaction variables are the reactor temperature and pressure and the nitrogen and sulfur content of the feed and off-gases. A summary of typical operating conditions and utility data is given below:[59,60]

- Pressure: 1,000 to 4,000 psig.
- Temperature: 400 to 850°F.
- Hydrogen recycle: 8,000 to 15,000 scf/bbl feed.
- Hydrogen consumption: 1,500 to 2,500 scf/bbl feed.
- Fuel: 100 to 250 × 10^3 Btu/bbl feed.

TABLE 7-18. TYPICAL EMISSIONS FROM CATALYTIC CRACKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	2
- Residual oil		
Grade 4	7	7
Grade 5	10	10
Grade 6	10(S)+3	10(S)+3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	145(S)
- Residual oil	157(S)	160(S)
Sulfur Trioxide[c]	2(S)	2(S)
Carbon Monoxide[d]	5	5
Hydrocarbons (as CH_4)[d]	1	1
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	22
- Residual oil[e]	$22+400(N)^2$	$22+409(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.7-2.0
Sulfur Oxides (as SO_2)[f]	0.6	0.08
Carbon Monoxide	17	2.3
Hydrocarbons (as CH_4)	3	0.41
Nitrogen Oxides (as NO_2)	120-230	16-31

[a] Source: Reference 7.

[b] Based on a heat input of 100,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-19. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL CATALYTIC CRACKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	384	849	0.059	22.7 - 50.1
	Light Liquid (VP > 0.1 psia @ 100°F)	409	889	0.024	9.82 - 21.3
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	521	1167	0.0005	0.261 - 0.584
	Hydrogen Service	0	0	0.018	0.0
	Total	1314[a]	2905[c]		32.8 - 72.0
Open-End (Sample) Valves	All	-	67[b]	0.005	0.335
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	16(22)	0.25	4.5 - 5.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	17(24)	21(29)	0.046	1.10 - 1.33
	Total	30(42)[a]	37(52)[b]		5.60 - 6.83
Drains	All	65[a]	-	0.070	4.55
Flanges & Fittings	All	4214[a]	9635[c]	0.00056	2.36 - 5.40
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	4(8)	4(8)	1.4	11.2
	Hydrogen	0	0	0.11	0.0
	Total	4(8)[a]	4(8)[b]		11.2
					58.0 - 101

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

TABLE 7-20. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A FLUID CATALYTIC CRACKING UNIT[a]

	Stream						
	Atmospheric Gas Oil	Fuel Gas	LPG Olefins	Cracked Naphtha	Lt. Cycle Gas Oil	Hvy. Cycle Gas Oil	Totals
Estimated percentage of emissions attributed to each stream - %	1	30	23	45	1	0	100%
Weighted contribution of each component to unit emissions - ppmw[b]							
Benzene	0	0	0	1296	0	0	1296
Toluene	0	0	0	40401	0	0	40401
Ethylbenzene	0	0	0	9644	0	0	9644
Xylenes	0	0	0	77153	6	0	77159
Other Alkylbenzenes	1	0	0	109562	267	0	109830
Naphthalene	0	0	0	4928	590	0	5518
Anthracene	0	0	0	0	103	0	103
Biphenyl	0	0	0	0	102	0	102
Other Polynuclear Aromatics	2	0	0	2916	6245	0	9163
n-Hexane	0	0	0	5324	0	0	5324
Other Alkanes	9495	216000	92000	91850	1906	0	471251
Olefins	0	18000	138000	76833	368	0	233201
Cyclo Alkanes	500	0	0	30096	412	0	31008
Hydrogen	0	6000	0	0	0	0	6000
							1000000

[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

- Power: 6 to 15 kWh/bbl feed.

- Space velocity: 0.2 to 1.0 v/hr/v.

Atmospheric Emissions--Emissions from hydrocracking include emissions during periodic catalyst regeneration, process heater flue gas emissions, and fugitive emissions.

During regeneration large quantities of carbon monoxide and other pollutants may be released, but, because regeneration may only be required after several months or years of operation, total averaged emissions from this source are generally insignificant.

Process heater and fugitive emissions are summarized in Tables 7-21 and 7-22.

7.1.4 Hydroprocessing

Hydroprocessing refers to those processes in which hydrogen is mixed with a variety of feedstocks and passed over a catalyst at elevated temperature and pressure. The hydrogen reacts with sulfur and nitrogen containing compounds in the feedstock to form hydrogen sulfide and ammonia. Heavy metals, oxygen and halides are also removed via hydroprocessing. Hydroprocessing may also be used to stabilize unsaturated hydrocarbons such as olefins by converting them to saturated materials.

Hydroprocessing operations may be divided into three categories, according to the severity of the process: (1) hydrocracking, in which 50 percent or more of the feed is reduced in molecular weight; (2) hydrorefining, in which 10 percent or less of the feed is reduced in molecular weight; and (3) hydrotreating, in which essentially no reduction in molecular weight occurs.

TABLE 7-21. TYPICAL EMISSIONS FROM HYDROCRACKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	2.9
- Residual oil		
Grade 4	7	10
Grade 5	10	14
Grade 6	10(S)+3	14(S)+4.3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	203(S)
- Residual oil	157(S)	224(S)
Sulfur Trioxide[c]	2(S)	2.9(S)
Carbon Monoxide[d]	5	7.1
Hydrocarbons (as CH_4)[d]	1	1.4
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	31
- Residual oil[e]	$22+400(N)^2$	$31+571(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.95-2.9
Sulfur Oxides (as SO_2)[f]	0.6	0.11
Carbon Monoxide	17	3.2
Hydrocarbons (as CH_4)	3	0.57
Nitrogen Oxides (as NO_2)	120-230	22.9-43.8

[a] Source: Reference 7.

[b] Based on a heat input of 200,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-22. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROCRACKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	175	0.059	10.3
	Light Liquid (VP > 0.1 psia @ 100°F)	375	0.024	9.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	307	0.0005	0.154
	Hydrogen Service	75	0.018	1.35
	Total	931[a]		20.8
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	12(17)	0.25	4.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	10(14)	0.046	0.644
	Total	22(31)[a]		4.9
Drains	All	58[a]	0.070	4.1
Flanges & Fittings	All	1955[b]	0.00056	1.09
Relief Valves	All	6[b]	0.19	1.1
Compressors (Compressor Seals)	Hydrocarbon	0(0)	1.4	0.0
	Hydrogen	3(6)	0.11	0.66
	Total	3(6)[a]		0.7
				32.7

[a] Physically Counted

[b] Estimated

Hydrocracking is discussed in Section 7.1.3. The following sections describe hydrorefining and hydrotreating processes.

7.1.4.1 Hydrorefining

Hydrorefining is used primarily for reducing the sulfur, nitrogen, or metal content of heavy feedstocks for further processing, blending, or direct use. Hydrodesulfurization is particularly important for catalytic cracking feeds.

The mechanism of the hydrorefining process is essentially the same as that for one-stage hydrocracking, discussed in Section 7.1.3.2, except that the emphasis is on removal of H_2S and NH_3 and cracking conditions are much less severe.

Process Conditions--Process conditions for hydrorefining vary with the feedstock and the desired products. A range of typical conditions and utility requirements is given below.

- Temperature: 390 to 800°F.
- Pressure: 500 to 800 psig.
- Electricity: 19 to 365 kWh/bbl.
- Heater Fuel: 0 to 70,000 Btu/bbl.
- Steam: 1 to 10 lb/bbl.
- Cooling Water: 160 gal/bbl.

Atmospheric Emissions--Emissions from hydrorefining operations include emissions during catalyst regeneration, process heater flue gas emissions, and fugitive emissions.

During catalyst regeneration, large quantities of carbon monoxide and other pollutants may be released. However, regeneration may be required only after several months or years of operation. Therefore, total averaged emissions from this source are generally considered insignificant.

Fugitive emissions and those from process heaters are summarized in Tables 7-23, 7-24 and 7-25.

7.1.4.2 Hydrotreating

Hydrotreating operations are less severe than hydrorefining processes. As in hydrorefining, hydrotreating is used to remove sulfur, nitrogen, and metallic compounds from the feed. It is also used to saturate olefins and aromatics and to polish and dewax lube oil stocks.

The mechanism of hydrotreating processes is essentially the same as that for one-stage hydrocracking, discussed in Section 7.1.3.2, except that cracking conditions are even less severe than those for hydrorefining. The product may be fractionated or steam-stripped to remove H_2S, NH_3, and light hydrocarbons.

Process Conditions--Operating conditions for hydrotreating vary with the feedstock and with the desired product. Typical operating conditions and utility requirements for three types of hydrotreating are given in Table 7-26.

Atmospheric Emissions--Emissions from hydrotreating include emissions during catalyst regeneration, process heater flue gas emissions, and fugitive emissions.

TABLE 7-23. TYPICAL EMISSIONS FROM GAS OIL HYDRODESULFURIZATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	**Total Emissions**[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	0.86
- Residual oil		
Grade 4	7	3.0
Grade 5	10	4.3
Grade 6	10(S)+3	4.3(S)+1.3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	60.9(S)
- Residual oil	157(S)	67.3(S)
Sulfur Trioxide[c]	2(S)	0.86(S)
Carbon Monoxide[d]	5	2.1
Hydrocarbons (as CH_4)[d]	1	0.43
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	9.4
- Residual oil[e]	$22+400(N)^2$	$9.4+171(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.29-0.86
Sulfur Oxides (as SO_2)[f]	0.6	0.034
Carbon Monoxide	17	0.97
Hydrocarbons (as CH_4)	3	0.17
Nitrogen Oxides (as NO_2)	120-230	6.86-13.1

[a] Source: Reference 7.

[b] Based on a heat input of 60,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE 7-24. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL GAS OIL HYDRODESULFURIZATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	235	205	0.059	13.9 - 12.1
	Light Liquid (VP > 0.1 psia @ 100°F)	208	244	0.024	4.99 - 5.86
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	102	97	0.0005	0.049- 0.051
	Hydrogen Service	101	164	0.018	1.82 - 2.95
	Total	645[a]	710[c]		20.8 - 21.0
Open-End (Sample) Valves	All	-	16[b]	0.005	0.080
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	6(9)	5(7)	0.25	1.75 - 2.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	4(5)	2(3)	0.046	0.14 - 0.23
	Total	10(14)[a]	7(10)[b]		1.89 - 2.48
Drains	All	24[a]	-	0.070	1.68
Flanges & Fittings	All	2743[a]	2350[c]	0.00056	1.44 - 1.54
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)[b]		0.66
					27.7 - 28.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

TABLE 7-25. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A GAS OIL HYDRODESULFURIZATION UNIT[a]

	Stream			
	Gas Oil	Desulfurized Gas Oil	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	22	22	56	100%
Weighted contribution of each component to unit emissions - ppmw[b]				
Benzene	0	0	0	0
Toluene	1	1	0	2
Ethylbenzene	1	1	0	2
Xylenes	5	5	0	10
Other Alkylbenzenes	8	81	0	162
Naphthalene	6	6	0	12
Anthracene	2	2	0	4
Biphenyl	2	2	0	4
Other Polynuclear Aromatics	146	146	0	292
n-Hexane	0	0	0	0
Other Alkanes	208756	208756	364000	781512
Olefins	0	0	0	0
Cyclo Alkanes	11000	11000	0	22000
Hydrogen	0	0	196000	196000
				1000000

[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

TABLE 7-26. TYPICAL OPERATING CONDITIONS FOR THREE HYDROTREATING OPERATIONS

Condition	Process		
	Light Hydrocarbon Hydrodesulfurization	Olefin/Aromatics Saturation	Lube and Wax Hydrotreating
Temperature, °F	600-800	480-660	600-750
Pressure, psig	300-1,000	100-1,500	500-700
Electricity, kWh/bbl	2.6	0.5-2.5	2.5
Heater Fuel, Btu/bbl	36,000-75,000	1,000	35,000-140,000
Cooling Water, gal/bbl	264	120-680	
Steam, lb/bbl	30-90[a]	12-35	15-30

[a] 30 to 90 lb/bbl with steam stripper, 5 lb/bbl without steam stripper.

During regeneration, large quantities of carbon monoxide and other pollutants may be released. However, regeneration may be required only after several months or years of operation. Therefore, total averaged emissions from this source are generally considered insignificant.

Fugitive emissions and emissions from process heaters are summarized in Tables 7-27, 7-28 and 7-29.

7.1.5 Conversion Processes

Conversion processes use catalyzed chemical reactions to upgrade certain refinery streams or to produce valuable products from less valuable materials. Conversion processes include alkylation, isomerization, catalytic reforming, and hydrodealkylation.

7.1.5.1 Alkylation

Alkylation is the chemical combination of an olefin and an isoparaffin, usually isobutane, to produce higher molecular weight isoparaffins. The alkylate product is usually used to upgrade the octane rating of gasoline. Almost all alkylation units use H_2SO_4 or HF as a catalyst.

Process Conditions--The most important variables in alkylation are reactor temperature, acid strength, isobutane concentration, and, in sulfuric acid alkylation, the olefin space velocity. Ranges for these and other variables are included in Table 7-30.

TABLE 7-27. TYPICAL EMISSIONS FROM HYDROTREATING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.1
- Residual oil		
Grade 4	7	3.8
Grade 5	10	5.4
Grade 6	10(S)+3	5.4(S)+1.6
Sulfur Dioxide[c]		
- Distillate oil	142(S)	76.1(S)
- Residual oil	157(S)	84.1(S)
Sulfur Trioxide[c]	2(S)	1.1(S)
Carbon Monoxide[d]	5	2.7
Hydrocarbons (as CH_4)[d]	1	0.54
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	12
- Residual oil[e]	$22+400(N)^2$	$12+214(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.36-1.1
Sulfur Oxides (as SO_2)[f]	0.6	0.043
Carbon Monoxide	17	1.2
Hydrocarbons (as CH_4)	3	0.21
Nitrogen Oxides (as NO_2)	120-230	8.6-16.4

[a] Source: Reference 7.

[b] Based on a heat input of 75,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE 7-28. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROTREATING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	235	226 - 389	0.059	13.3 - 23.0
	Light Liquid (VP > 0.1 psia @ 100°F)	208	378 - 648	0.024	4.99 - 15.6
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	102	0	0.0005	0.0 - 0.051
	Hydrogen Service	101	181 - 312	0.018	1.82 - 5.62
	Total	645[a]	785 - 1349[c]		20.1 - 44.3
Open-End (Sample) Valves	All	-	17 - 29[b]	0.005	0.085- 0.145
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	6(9)	8(11)-16(22)	0.25	2.25 - 5.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	4(5)	0	0.046	0.0 - 0.23
	Total	10(14)[a]	8(11)-16(22)[b]		2.25 - 5.73
Drains	All	24[a]	-	0.070	1.68
Flanges & Fittings	All	2743[a]	2585 - 4465[c]	0.00056	1.44 - 2.50
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)[b]		0.66
					27.4 - 56.0

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

TABLE 7-29. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A HYDROTREATING UNIT[a]

	Stream			
	Straight Run Naphtha	Desulfurized Naphtha	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	47	47	6	100%
Weighted contribution of each component to unit emissions - ppmw[b]				
Benzene	119	119	0	238
Toluene	1232	1232	0	2464
Ethylbenzene	417	417	0	834
Xylenes	763	763	0	1526
Other Alkylbenzenes	7792	7792	0	15584
Naphthalene	688	688	0	1376
Anthracene	2	2	0	4
Biphenyl	295	295	0	590
Other Polynuclear Aromatics	7042	7042	0	14084
n-Hexane	18254	18254	0	36508
Other Alkanes	234817	234817	39000	508634
Olefins	0	0	0	0
Cyclo Alkanes	198579	198579	0	397158
Hydrogen	0	0	21000	21000
				1000000

[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

TABLE 7-30. TYPICAL OPERATING CONDITIONS FOR ALKYLATION OPERATIONS

Condition	Process H_2SO_4 Alkylation	 HF Alkylation
Reactor Temperature, °F	35 - 60	60 - 120
Acid Strength, Wt. %	88 - 95	83 - 92
Acid in Emulsion, Wt. %	40 - 60	25 - 80
Olefin Space Velocity, v/hr/v	0.1 - 0.6	---
Isobutane Concentration, Vol %	40 - 80	30 - 80
Steam, lb/bbl alkylate	300 - 400	---
Power, kWh/bbl alkylate	2.5 - 5	3 - 7
Fuel, 10^6 Btu/bbl alkylate	---	0.3 - 1.1

Source: References 38,50,51,61.

Potentially Hazardous Atmospheric Emissions--The alkylation process is a closed system; therefore, the only emissions are those associated with process heating and fugitive emissions. These emissions are summarized in Tables 7-31, 7-32 and 7-33.

7.1.5.2 Isomerization

Isomerization processes convert normal paraffins into isoparaffins. In general, octane numbers are much higher for isoparaffins than for normal paraffins. The process is also used to produce isobutane for use in alkylation units.

Process Conditions--Temperature is a critical factor in isomerization reactions. In general, equilibrium concentrations of isoparaffins are increased by reducing the reaction temperature. Typical process conditions and utility requirements for both the vapor phase-solid catalyst system described earlier and the liquid phase system are given in Table 7-34.

TABLE 7-31. TYPICAL EMISSIONS FROM ALKYLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of total alkylate)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	5.1
- Residual oil		
Grade 4	7	18
Grade 5	10	26
Grade 6	10(S)+3	26(S)+7.7
Sulfur Dioxide[c]		
- Distillate oil	142(S)	365(S)
- Residual oil	157(S)	404(S)
Sulfur Trioxide[c]	2(S)	5.1(S)
Carbon Monoxide[d]	5	13
Hydrocarbons (as CH_4)[d]	1	2.6
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	57
- Residual oil[e]	$22+400(N)^2$	$57+1030(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.7-5.1
Sulfur Oxides (as SO_2)[f]	0.6	0.21
Carbon Monoxide	17	5.8
Hydrocarbons (as CH_4)	3	1.0
Nitrogen Oxides (as NO_2)	120-230	41.1-78.9

[a] Source: Reference 7.

[b] Based on a heat input of 360,000 Btu/bbl of total alkylate with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE 7-32. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL SULFURIC ACID ALKYLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	274	429 - 719	0.059	16.2 - 42.4
	Light Liquid (VP > 0.1 psia @ 100°F)	403	636 - 1067	0.024	9.67 - 25.6
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0	0	0.0005	0.0
	Hydrogen Service	0	0	0.018	0.0
	Total	677[a]	1065 - 1786[c]		25.9 - 68.0
Open-End (Sample) Valves	All	-	26 - 30[b]	0.005	0.13 - 0.15
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	13(18)-23(32)	0.25	4.50 - 8.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0(0)	0(0)- 0(0)	0.046	0.0
	Total	13(18)[a]	13(18)-23(32)[b]		4.50 - 8.00
Drains	All	41[a]	-	0.070	2.87
Flanges & Fittings	All	2407[a]	3525 - 5875[c]	0.00056	1.35 - 3.29
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0(0) - 2(4)	1.4	0.0 - 5.60
	Hydrogen	0	0(0) - 0(0)	0.11	0.0
	Total	0	0(0) - 2(4)[b]		0.0 - 5.60
					35.9 - 89.1

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

TABLE 7-33. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM AN ALKYLATION UNIT[a]

	Stream				
	LPG Olefins	LPG	H_2SO_4	Alkylate	Totals
Estimated percentage of emissions attributed to each stream - %	24	35	0	41	
Weighted contribution of each component to unit emissions - ppmw[b]					
Benzene	0	0	0	0	0
Toluene	0	0	0	0	0
Ethylbenzene	0	0	0	0	0
Xylenes	0	0	0	1	1
Other Alkylbenzenes	0	0	0	1	1
Naphthalene	0	0	0	0	0
Anthracene	0	0	0	0	0
Biphenyl	0	0	0	0	0
Other Polynuclear Aromatics	0	0	0	1	1
n-Hexane	0	0	0	39	39
Other Alkanes	96000	350000	0	409572	855572
Olefins	144000	0	0	381	144381
Cyclo Alkanes	0	0	0	5	5
					1000000

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[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

TABLE 7-34. OPERATING CONDITIONS AND UTILITY REQUIREMENTS FOR PARAFFINS ISOMERIZATION PROCESSES

	Solid Bed Systems	Liquid Phase Systems
Reactor Temperature, °F	200 - 600	150 - 250
Reactor Pressure, psig	200 - 1,000	300 - 500
Liquid Space Velocity, v/hr/v	1 - 4	2 - 3
Fuel, 10^3 Btu/bbl feed	10 - 50	NA[a]
Electricity, kWh/bbl feed	1 - 2	NA[a]

Source: References 38,50,51,61,62,63.

[a] NA = not available

Atmospheric Emissions--An isomerization unit is a closed system. The emission sources for this process are process heater flue gas and fugitive emissions. Emissions from process heaters are summarized in Table 7-35. Fugitive emissions are estimated in Table 7-36.

7.1.5.3 Catalytic Reforming

Catalytic reforming is one of the most important of all refinery processes. In catalytic reforming, relatively low octane naphthas are converted to highly aromatic, high octane gasoline blending stocks. The reforming operation consists basically of contacting oil and hydrogen with a catalyst in a series of three to six reactors. Because the overall reaction is endothermic, the mixture must be heated before it is charged to each reactor.

A number of reactions occur simultaneously during the reforming process including dehydrogenation, isomerization, and hydrocracking. Dehydrogenation reactions which result in the formation of aromatics are the most important.

TABLE 7-35. TYPICAL EMISSIONS FROM ISOMERIZATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	0.71
- Residual oil		
Grade 4	7	2.5
Grade 5	10	3.6
Grade 6	10(S)+3	3.6(S)+1.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	50.7(S)
- Residual oil	157(S)	56.1(S)
Sulfur Trioxide[c]	2(S)	0.71(S)
Carbon Monoxide[d]	5	1.8
Hydrocarbons (as CH_4)[d]	1	0.36
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	7.9
- Residual oil[e]	$22+400(N)^2$	$7.9+143(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.24-0.71
Sulfur Oxides (as SO_2)[f]	0.6	0.029
Carbon Monoxide	17	0.81
Hydrocarbons (as CH_4)	3	0.14
Nitrogen Oxides (as NO_2)	120-230	5.71-11.0

[a] Source: Reference 7.

[b] Based on a heat input of 50,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-36. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL BUTANE ISOMERIZATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	238	0.059	14.0
	Light Liquid (VP > 0.1 psia @ 100°F)	310	0.024	7.44
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0	0.0005	0.0
	Hydrogen Service	102	0.018	1.84
	Total	650[a]		23.3
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	10(14)	0.25	3.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0(0)	0.046	0.0
	Total	10(14)[a]		3.50
Drains	All	26[a]	0.070	1.82
Flanges & Fittings	All	2321[a]	0.00056	1.30
Relief Valves	All	6[a]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	1.4	0.0
	Hydrogen	2(4)	0.11	0.44
	Total	2(4)[a]		0.44
				31.5

[a] Estimated

Catalytic reforming processes are categorized by the method or frequency of catalyst regeneration. Catalyst beds may be regenerated continuously, all at once at the end of a 3 to 24-month cycle (semi-regeneration), or one at a time while an alternate "swing" reactor is in use (cyclic regeneration). The method of regeneration affects the choice of catalyst and the product yields obtainable.

Process Conditions--A summary of typical operating conditions and utility requirements for catalytic reforming is given below.[38,50,51]

- Reactor temperature: 850 to 1,000°F.
- Reactor pressures
  Semi-regeneration: 150 to 500 psig.
  Cyclic regeneration: 90 to 200 psig.
  Continuous regeneration: 90 to 200 psig.
- Space velocity: 1.5 to 3.0 v/hr/v.
- Power: 5 to 7 kWh/bbl.
- Fuel: 0.15 to 0.32 × 10^6 Btu/bbl feed.

Atmospheric Emissions--Emissions from catalytic reforming include emissions from catalyst regeneration, process heater flue gas, and fugitive emissions. During the reforming operation, coke is deposited on the catalyst. The rate of coke formation is a function of the type of feedstock and the severity of the operating conditions. During regeneration a flue gas stream is generated which contains carbon monoxide and low concentrations of sulfur and nitrogen oxides.

Total averaged emissions from catalyst regeneration are quite low because only small amounts of coke are produced and the frequency of regeneration may be low. These emissions are highest for continuous operations because more severe operating conditions can be used. Carbon monoxide emissions from continuous reformers have been estimated at 0.002 to 0.02 pounds per barrel of fresh feed, a relatively small amount.

Emissions from process heaters and fugitive emissions are summarized in Tables 7-37, 7-38, and 7-39.

7.1.5.4 Hydrodealkylation

Hydrodealkylation removes alkyl groups from aromatic rings at elevated temperatures in the presence of hydrogen. The reaction can be conducted either thermally or in the presence of a catalyst.

Since hydrodealkylation is a closed process, the only emissions are fugitive emissions and emissions from process heaters. These emissions are summarized in Tables 7-40 and 7-41.

7.1.6 Gas Processing [64,65,66,67,68,69]

Gas processing recovers various hydrocarbons as pure products or as mixtures of specified compositions. The products of gas processing may be fuel gas, methane, ethane, propane, propylene, normal and isobutane, butylenes, normal and isopentane, amylene, and/or a light naphtha.

The feed to gas processing units comes from crude distillation, catalytic reforming, catalytic cracking, hydrocracking, thermal cracking, and to a lesser extent, hydrodesulfurization. Major units include acid gas removal, dehydration, and separation.

TABLE 7-37. TYPICAL EMISSIONS FROM CATALYTIC REFORMING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	2.9
- Residual oil		
Grade 4	7	10
Grade 5	10	14
Grade 6	$10(S)+3$	$14(S)+4.3$
Sulfur Dioxide[c]		
- Distillate oil	142(S)	203(S)
- Residual oil	157(S)	224(S)
Sulfur Trioxide[c]	2(S)	2.9(S)
Carbon Monoxide[d]	5	7.1
Hydrocarbons (as CH_4)[d]	1	1.4
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	31
- Residual oil[e]	$22+400(N)^2$	$31+571(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.95-2.9
Sulfur Oxides (as SO_2)[f]	0.6	0.11
Carbon Monoxide	17	3.2
Hydrocarbons (as CH_4)	3	0.57
Nitrogen Oxides (as NO_2)	120-230	22.9-43.8

[a] Source: Reference 7.

[b] Based on a heat input of 200,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE 7-38. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL CATALYTIC REFORMING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit: Counts or Estimates From Radian Study	Number of Sources in Process Unit: Counts or Estimates From PES Study[d]	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	180	154 - 291	0.059	9.09 - 17.2
	Light Liquid (VP > 0.1 psia @ 100°F)	391	493 - 938	0.024	9.38 - 22.5
	Heavy Liquid (VP $\le$ 0.1 psia @ 100°F)	43	0	0.0005	0.0
	Hydrogen Service	77	139 - 263	0.018	1.39 - 4.73
	Total	691[a]	786 - 1492[c]		19.9 - 44.4
Open-End (Sample) Valves	All	-	16 - 30[b]	0.005	0.080 - 0.15
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	8(11)-17(24)	0.25	2.75 - 6.00
	Heavy Liquid (VP $\le$ 0.1 psia @ 100°F)	1(2)	0	0.046	0.0 - 0.092
	Total	14(20)[a]	8(11)-17(24)[b]		2.75 - 6.09
Drains	All	49[a]	-	0.070	3.43
Flanges & Fittings	All	2961[a]	2585 - 4935[c]	0.00056	1.45 - 2.76
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)		0.66
					29.4 - 58.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

TABLE 7-39. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A CATALYTIC REFORMING UNIT[a]

	Stream			
	Desulfurized Naphtha	Reformate	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	47	47	6	100%
Weighted contribution of each component to unit emissions - ppmw[b]				
Benzene	119	2538	0	2657
Toluene	1232	36519	0	37751
Ethylbenzene	417	15745	0	16162
Xylenes	763	80323	0	81086
Other Alkylbenzenes	7792	152468	0	160260
Naphthalene	688	3478	0	4166
Anthracene	2	0	0	2
Biphenyl	295	0	0	295
Other Polynuclear Aromatics	7042	329	0	7371
n-Hexane	18254	11280	0	29534
Other Alkanes	234817	167320	39000	441137
Olefins	0	0	0	0
Cyclo Alkanes	198579	0	0	198579
Hydrogen	0	0	21000	21000
				1000000

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[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

TABLE 7-40. TYPICAL EMISSIONS FROM HYDRODEALKYLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	**Total Emissions**[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	4.1
- Residual oil		
Grade 4	7	15
Grade 5	10	21
Grade 6	10(S)+3	21(S)+6.2
Sulfur Dioxide[c]		
- Distillate oil	142(S)	294(S)
- Residual oil	157(S)	325(S)
Sulfur Trioxide[c]	2(S)	4.1(S)
Carbon Monoxide[d]	5	10
Hydrocarbons (as CH_4)[d]	1	2.1
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	46
- Residual oil[e]	$22+400(N)^2$	$46+829(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.4-4.1
Sulfur Oxides (as SO_2)[f]	0.6	0.17
Carbon Monoxide	17	4.7
Hydrocarbons (as CH_4)	3	0.83
Nitrogen Oxides (as NO_2)	120-230	33.1-63.5

[a] Source: Reference 7.

[b] Based on a heat input of 290,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE 7-41. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDRODEALKYLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	179	116	0.059	6.84 - 10.6
	Light Liquid (VP > 0.1 psia @ 100°F)	391	352	0.024	8.45 - 9.38
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	43	0	0.0005	0.0 - 0.022
	Hydrogen Service	77	100	0.018	1.39 - 1.80
	Total	690[b]	568[b]		16.7 - 21.8
Open-End (Sample) Valves	All	-	10[a]	0.005	0.05
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	6(8)	0.25	2.00 - 4.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	1(2)	0(0)	0.046	0.0 - 0.092
	Total	14(20)[b]	6(8)[a]		2.00 - 4.59
Drains	All	36[b]	-	0.070	2.52
Flanges & Fittings	All	2463[b]	1880[b]	0.00056	1.05 - 1.38
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	2(4)	0.11	0.44 - 0.66
	Total	3(6)	2(4)[a]		0.44 - 0.66
					23.9 - 32.1

[a] Counted from Flow Diagrams

[b] Estimated

[c] Reference 49

7.1.6.1 Acid Gas Removal

The acid gas removal unit removes hydrogen sulfide from hydrocarbon gases, usually by absorption in an aqueous, regenerative sorbent. CO_2 and/or mercaptans may also be removed, depending on the process used.

A number of acid gas removal processes are available, distinguished primarily by the regenerative sorbent used. Amine-based sorbents are most commonly used.

The feed to a typical unit is contacted with the sorbent, such as diethanolamine, in an absorption column to selectively absorb H_2S from the hydrocarbon gases. Hydrogen sulfide is then removed from the sorbent in a regeneration step. The products are a sweet hydrocarbon gas and a concentrated hydrogen sulfide stream. The hydrogen sulfide stream is normally routed to a sulfur plant for recovery of its sulfur content. Alternatively, the sulfide gas may be flared to produce the less toxic sulfur oxides.

Process Conditions--A typical absorber operates at a pressure of about 150 psi and a temperature of about 100°F. Pressure and temperature may, in some instances, be significantly higher.

Atmospheric Emissions--If a regenerative sorbent system is used in conjunction with a sulfur recovery unit, only fugitive emissions are produced. If the hydrogen sulfide stream is flared, sulfur oxide emissions are produced.

7.1.6.2 Dehydration

Dehydration removes water from the gas after the acid gas removal step. Excess water may be removed by refrigeration, absorption, or adsorption. Refrigeration processes decrease the temperature to below the required dew point; condensed moisture is collected for disposal.

Absorption processes allow the moist gas to flow over a hygroscopic material such as di- or triethylene glycol. Solid dissicants such as silica gel or alumina are used in adsorption processes. Beds are regenerated with hot gas.

Process Conditions--Temperature and pressure are interdependent in condensation processes. For example, if the required dew point is 50°F at 135 psig and the best available cooling is 90°F, the pressure will be 460 psig.

For absorption processes using di- or triethylene glycol, absorption temperatures must be kept below the glycol's decomposition temperature (327°F for DEG, 405°F for TEG). Temperatures in the regenerator, where water is separated from the glycol, usually range from 375° to 400°F.

Regeneration temperatures for solid dessicants are 480° to 500°F.

Utilities--A glycol absorption process requires about 0.1 percent of the fuel produced.

Atmospheric Emissions--An estimated 0.1 gallon of triethylene glycol per 10 ft^3 of gas processed is emitted by a glycol absorption unit in vented water vapor. Water contaminated with glycol may be vented as steam or it may be disposed of as a liquid. Hydrocarbons may also be emitted from fugitive sources.

7.1.6.3 Product Separation/LPG Production

Refinery gas is often separated into its components in a gas separation plant. This separation is usually accomplished by contacting the gas with an absorber oil. Refrigerated absorption, refrigeration, or adsorption may be used when a separate methane stream is desired.

In the oil absorption process, the gas is contacted with an absorber oil in a packed or bubble tray column. Propane and heavier hydrocarbons are absorbed by the oil while most of the methane and ethane pass through the absorber. The enriched absorber oil is then taken to a stripper where the absorbed propane and heavier compounds are stripped from the oil.

In the refrigeration process, the gas is first dried with molecular sieve beds. It is then cooled in a heat exchanger to - 25°F. Condensed hydrocarbons are removed in a gas-liquid separator. The gas from this separator is passed through a second separator at - 135°F. Liquids from the separators are fed to a series of distillation columns where methane, ethane, propane, butane, and other products are recovered.

An activated carbon bed adsorbs all hydrocarbons except methane. The bed is regenerated with heat and steam; the resulting hydrocarbon vapor is condensed and the water separated. The resulting hydrocarbon product is then fractionated into its various components.

Process Conditions--Pressure in an oil absorber may be as high as 400 psi, but is usually lower. Inlet gas and oil temperatures are 90° to 100°F.

Emissions--Fugitive emissions from leaking pumps, valves, compressors, and other fittings are the only emissions from product separation.

7.1.7 Other Processes

7.1.7.1. Asphalt Processing/Production

Asphalt is produced as the bottoms from vacuum distillation, discussed in Section 7.1.1.2. The removal of lube oil by deasphalting is discussed in Section 7.1.7.4.

The quality of asphalt is improved by blowing air through it (air-blowing) to increase its melting temperature and hardness. Both batch and continuous processes are used. Catalysts such as ferric chloride or phosphorus pentoxide are sometimes used.

Because asphalt is distilled before it reaches the air-blowing process, hydrocarbon emissions from the process are relatively minor. Available data indicate that uncontrolled emissions from air-blowing of asphalt are about 60 pounds per ton of asphalt.[70] The operating conditions are favorable for the production of extremely undesirable polynuclear aromatics.

In some refineries, air-blown units have been replaced with vessels packed with solid absorbents. These vessels have no emissions other than fugitive emissions.

7.1.7.2 Blending

Products with desired characteristics are often made by the mixing of various components. The most common blending operation in petroleum refining is the manufacture of gasoline.

Blending may be by batch or in-line. Batch blending takes place in a blending tank to which components are added individually. Agitation may be either by an external circulation loop or by internal impellers powered by external motors.

In-line blending may be partial or continuous. Partial blending involves simultaneous combination of stock components in a mixing manifold. Final additions are made downstream or in a storage tank. Continuous blending is the simultaneous blending of all components in a mixing manifold.

Fugitive emissions from batch blending tanks are often more than from similar storage tanks because of the agitation. Fugitive emissions from in-line blending are limited to fugitive leaks from valves, flanges, and other process equipment.

Control technology for batch blending operations includes floating roofs on blending tanks and replacement of batch operations with in-line blending operations.

7.1.7.3 Hydrogen Production

A refinery with a large distillate hydrotreater or gas oil hydrocracker requires more high-purity hydrogen than is supplied by other refinery processes. It is estimated that by 1980, slightly less than 40 percent of the hydrogen used in refineries will be manufactured within the refineries.[71]

Steam-hydrocarbon reforming is commonly used for hydrogen production, but because it uses valuable light hydrocarbons, it will probably be gradually replaced by partial oxidation of heavy oils. The choice between the two processes depends on the cost and availability of raw materials.[72]

Emissions from steam-hydrocarbon reforming are limited to those from process heaters and fugitive emissions. No specific information was available on emissions from partial oxidation. It is assumed they are confined to process heater emissions and fugitive emissions. Emissions from steam-hydrocarbon reforming are summarized in Tables 7-42 and 7-43. These emissions are more appropriate for units using liquid feedstocks. Those units utilizing natural gas as feed should have low emissions of nonmethane hydrocarbons.

7.1.7.4 Lube Oil Processing/Production

Lube oil stock is produced as the 700 to 1,000°F fraction of the residuum from vacuum distillation. Procedures for processing the lube oil stock into specific products vary greatly, but they can be divided into four groups: deasphalting, treating, dewaxing, and finishing.

Each of these processes is closed to the atmosphere. Except for hydrotreating, there are no emissions except for fugitive emissions and emissions from process heaters. With hydrotreating, there are emissions, particularly CO, associated with periodic catalyst regeneration.

Deasphalting--A very heavy oil (brightstock) can be produced from vacuum residues by extraction with propane at temperatures from 104 to 140°F. At these temperatures, paraffins are quite soluble in propane, but high molecular weight asphaltic and resinous compounds precipitate.

Propane can also be used to separate a lighter oil fraction (SAE 50), a very heavy oil, and hard asphalt by fractionation.

Treating--Several methods are used to improve the viscosity index, the color, and the carbon residue content of lube oil. The two most common treating methods are phase extraction and furfural treating. Hydrotreating has also been used.

TABLE 7-42. ESTIMATED FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROGEN PRODUCTION UNIT[e]

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	**Gas/Vapor**	19	244	0.059	1.12 - 14.4
	Light Liquid (VP > 0.1 psia @ 100°F)	93	2101	0.024	2.23 - 50.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	62	0	0.0005	0.0 - 0.031
	Hydrogen Service	8	122	0.018	0.14 - 2.20
	Total	182[a]	2467[c]		3.49 - 67.0
Open-End (Sample) Valves	**All**	--	46[b]	0.005	0.23
Pumps (Pump Seals)	**Light Liquid** (VP > 0.1 psia @ 100°F)	3(4)	2(3)	0.25	0.75 - 1.0
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	2(3)	0(0)	0.46	0.0 - 0.138
	Total	5(7)[a]	2(3)[b]		0.75 - 1.14
Drains	**All**	17[c]	--	0.070	1.19
Flanges & Fittings	**All**	635[a]	8225[c]	0.00056	0.36 - 4.61
Relief Valves	**All**	6[c]	--	0.19	1.14
Compressors (Compressor Seals)	**Hydrocarbon**	0(0)	0(0)	0.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[c]	3(6)[b]		0.66
					7.82 - 75.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 49.

[e] Light Liquid Hydrocarbon Feedstock

TABLE 7-43. ESTIMATED COMPOSITION OF FUGITIVE EMISSIONS FROM A HYDROGEN PRODUCTION UNIT UTILIZING NAPHTHA AS FEEDSTOCK[a]

	Streams				
	Fuel Gas	Straight Run Naphtha	LPG	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - wt %	38	19	19	24	100%
Weighted contribution of each component to unit emissions ppmw[b]					
Benzene	0	48	0	0	48
Toluene	0	498	0	0	490
Ethylbenzene	0	169	0	0	169
Xylenes	0	308	0	0	308
Other Alkylbenzenes	0	3150	0	0	3150
Naphthalene	0	278	0	0	278
Anthracene	0	1	0	0	1
Biphenyl	0	119	0	0	119
Other Polynuclear Aromatics	0	2847	0	0	2847
n-Hexane	0	7379	0	0	7379
Other Alkanes	349600	94926	190000	156000	790526
Olefin	22800	0	0	0	22800
Cycloalhanes	0	80277	0	0	80277
Hydrogen	7600	0	0	84000	91600
					1,000,000

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[a] Based on GC-MS analysis of liquid stream samples (and some vapor samples). Estimates based on the assumption that fugitive emission compositions from sources in liquid stream service is the same composition as that of the liquid contained in the emission source.

[b] Compositions are estimated to 2-3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

Dewaxing--Dewaxing is the most difficult part of lube oil manufacture. The oil is contacted with solvent and chilled, causing the wax to precipitate. The precipitated wax is separated from the mixture by filtration or centrifugation. The dewaxed oil and solvent are separated by distillation and steam stripping. The wax is solvent treated again under different conditions to obtain a deoiled wax product.

Finishing--Finishing processes remove traces of resinous materials and chemically active compounds which can deteriorate the color of the product. The compounds can be absorbed by contacting the oil with various types of clay, activated earth, or artificial absorbents. Hydrotreating (hydrofinishing) can also be used to effectively remove nitrogen compounds which cause the oil to darken and become unstable. Sulfur and oxygen content are also effectively reduced by hydrofinishing.

7.1.7.5 Sulfur Recovery

A sulfur recovery plant converts hydrogen sulfide to elemental sulfur. The Claus process is assumed to be used for sulfur recovery by all major refiners.

Process types and process flow diagrams for the Claus process are given in Appendix E (Volume 4). The amount of sulfur reaching the sulfur recovery unit varies with the percent sulfur in the crude and the extent of desulfurization. Typically, 60 percent of the sulfur in the crude reaches the sulfur recovery plant.

Process Conditions--A Claus plant operates at about 470°F and one to two atmospheres. About 20 Btu of heat are required per pound of sulfur produced. However, approximately four pounds of steam per pound of sulfur are produced in a waste heat boiler. This steam can provide from five to thirty percent of the total refining steam requirements.

Atmospheric Emissions--Process emissions from Claus plants are discussed in Appendix E (Volume 4). A 100,000 bpd refinery with a one percent sulfur crude and a 95 percent efficient sulfur plant will produce 5 - 6 tons/day of sulfur emissions. Sulfur is emitted as SO_2, H_2S, COS, CS_2, and mercaptans.

It is estimated that there are 200 valves, 800 flanges, nine pump seals, 20 drains, and four relief valves on a typical Claus unit. These can be sources of fugitive emissions of various sulfur compounds from the Claus unit. However, because sulfur compounds such as H_2S are present in streams, safety practices dictate careful attention to maintenance.

7.1.8 Waste Treatment

7.1.8.1 Blowdown/Flare

Blowdown/flare systems are common to all crude oil refineries. A blowdown system consists of pressure relief devices, manual bypass valves, blowdown headers, knockout vessels, and holding tanks. Compressors and vapor surge vessels may also be included. A flare is used for final disposal of noncondensable combustible gases.

A pressure relief valve is an automatic pressure-relieving device activated by the static pressure upstream of the valve. There are three types of pressure relief valves: relief valves, safety valves and safety-relief valves. Relief valves, used primarily for liquid service, open in proportion to the increase in pressure. Safety valves, used in the petroleum industry primarily for steam or air service, pop fully open at a set pressure. Safety-relief valves may be used as either safety valves or relief valves, depending on application.

Another pressure relief device, the rupture disk, consists of a thin metal diaphragm held between flanges. Rupture disks are sometimes installed upstream of pressure relief valves to prevent hydrocarbon leakage from valve seals.

Flares may be designed for emergency or routine use. These may be burning pits, elevated flares, or ground-level flares.

Burning pits are normally used only for emergency burning of large quantities of gases. A typical pit is simply an excavation 4 to 6 feet deep and 30 to 40 feet square with burners mounted on one wall. These are not commonly used in modern refineries. Elevated flares allow gases to be burned safely from the top of a stack. Ground flares are installed in a large open area for safety and fire protection.[46]

Smoke emissions from flares are avoided whenever possible. For smokeless operation, three combustion principles are followed: maintenance of critical combustion temperatures, adequate combustion air, and adequate mixing of air and fuel. Steam is often injected to provide turbulence which promotes mixing. Air and water have also been used. Further discussion of the use of steam in flares is provided in Appendix E (Volume 4) and Appendix F (Volume 5). Emissions from blowdown/flares include:

- Combustion products from flares.

- Fugitive emissions.

Emission factors for smokeless flares are given in Table 7-44. It should be noted that these flare emission factors may not be applicable to specific flares due to variations in off-gas composition, flow rate, and design configuration.

TABLE 7-44. EMISSIONS FROM SMOKELESS FLARES

Component	Emissions[a] (lb/10^3 bbl total refinery capacity)
Particulates	Negligible
SO_x[b]	26.9
CO	4.3
Hydrocarbons	0.8
NO_x	18.9
NH_3	Negligible
Aldehydes	Negligible

[a] Source: Reference 7.

[b] Varies with fuel sulfur content.

7.1.8.2 Wastewater Treatment

A tremendous quantity of water is used in a refinery. A substantial portion of this water is reused before discharge. However, it must normally be treated to remove contaminants before discharge.

Refinery wastewater treatment is of two types: inplant treatment (pretreatment) and end-of-pipe treatment. Inplant treatment is the use of procedures which can (1) reduce the amount of pollutants sent to the wastewater system, (2) reduce the amount of water discharged, and (3) make subsequent end-of-pipe treatment more effective. End-of-pipe treatment processes are classified as primary, intermediate, secondary, or tertiary processes, depending on their function.

High concentrations of hydrogen sulfide and ammonia are often reduced by steam-stripping before water is sent to the wastewater system. Phenol may be removed by using phenolic waters as desalter water: a portion of the phenol is **absorbed** by the crude oil.[45] Any technique which limits contact between oil and water also reduces the waste load.

A number of procedures have been developed to reduce the amount of wastewater. Among these are recirculation, use of air coolers and cooling towers to eliminate once-through cooling, and chemical treatment to prevent corrosion or scaling.

Pretreatment techniques which improve the efficiency of end-of-pipe treatment include stream segregation, preaeration of the water to meet immediate oxygen demand, and surge ponds to smooth the flow of wastewater. An example of refinery stream segregation in a modern refinery is given in Appendix F (Volume 5). Older refineries may be able to segregate only sanitary wastes.

A classification of end-of-pipe wastewater treatment processes is given in Table 7-45. Each refinery has its own particular scheme based on the type of refinery, the water use pattern, and applicable pollution regulations.

Primary treatment is often the only treatment required of a refinery. API separators remove oil which floats and coalesces on the surface of the water and sludge which settles to the bottom of the separator. Parallel plate separators are a relatively new method for removing oil and sludge which reduce the distance the oil droplets must travel before collection.

Intermediate treatment removes materials such as emulsions and suspended or colloidal solids, which neither float nor settle within the

TABLE 7-45. CLASSIFICATION OF END-OF-PIPE REFINERY WASTEWATER TREATMENT PROCESSES

Treatment	Objectives	Processes
Primary Treatment	Free Oil and Suspended Solids Removal	API Separators Parallel Plate Separators
Intermediate Treatment	Emulsified Oil, Suspended Solids, and Colloidal Solids Removal	Dissolved Air Flotation Coagulation-Flotation Coagulation-Precipitation Filtration Equalization
Secondary Treatment	Dissolved Organics Removal Reduction in BOD and COD	Activated Sludge Trickling Filters Aerated Lagoons Oxidation Ponds Rotating Biological Discs
Tertiary Treatment	Variable Objectives	Filtration Air Flotation Coagulation Activated Carbon

residence time provided in primary treatment. Removal may be by dissolved air flotation (DAF), chemical coagulation and sedimentation, or filtration.

Secondary treatment involves physical, biological, or chemical treatment for the removal of dissolved organics. Physical and chemical treatments are considered advanced treatment processes which follow biological treatment.

All of the biological methods for secondary wastewater treatment involve oxidative decomposition by micro-organisms. These processes--activated sludge, trickling filters, aerated lagoons, oxidation ponds, and rotating biological discs - are discussed in Appendix F (Volume 5).

Some refineries provide additional tertiary treatment downstream of biological treatment units. This polishing treatment may be necessitated by changes in refinery effluent water quality or by government regulations on effluent quality. Tertiary treatment commonly involves the reduction of suspended solids and carbon adsorption for removal of organic pollutants.

Fugitive emissions are released from all of the above operations. The extent of these emissions is a function of the amount and volatility of hydrocarbons entering a unit, emission controls used, and other factors. The greatest opportunities for emissions are at the front end of the wastewater system, i.e., sewers, open ditches, holding ponds prior to the API separator, and the API separator itself. Since the API separator removes most of the hydrocarbons with the skimmed oil, units downstream of it release substantially fewer fugitive hydrocarbons. Emission factors for API separators are given in Table 7-46. Emission rates could not be determined accurately enough to warrant the development of emission factors in this study. Data to update these factors will be collected as part of an EPA research program on petroleum refinery wastewater system emissions.

TABLE 7-46. API SEPARATOR EMISSION FACTORS

	Emissions	
	lb/10^3 gal Wastewater	lb/10^3 bbl Refinery Feed
API separators (uncontrolled)	5	200
API separators (controlled by fixed or floating roof)	0.2	10

Source: Reference 7.

7.1.8.3 Sludge/Solids Treating/Disposal

Many of the solid wastes generated by petroleum refineries contain toxic hydrocarbons or metallic compounds. The wastes may be generated continuously or intermittently.

Solid wastes have historically been sent directly to landfills or open pits for disposal. Oily wastes, although sometimes incinerated, have usually been sent to an oily waste disposal pit.

More stringent solid waste disposal regulations have forced the adoption of more advanced disposal practices. Landfilling is still the most commonly used method, but landfills must now be constructed to allow no direct contact between the waste and surface or groundwater.

Landfarming involves the use of soil bacteria to biodegrade organic materials in solid wastes. Little is known about the nature of the degradation products or about the fate of heavy metals or toxic organic compounds in the waste.[73]

Incineration is a relatively expensive method for solid waste treatment. Supplemental fuel, pollution controls, and dewatering of the waste may be required. And, although the waste volume is reduced, the incinerator ash must still be disposed.

Chemical fixation involves the addition of certain chemicals to a waste to form an insoluble solid which can be landfilled. Little leaching of heavy metals and organic compounds results from chemically fixed waste.[74]

7.2 Control Technology

Refinery control technology includes all types of equipment, processes, operating practices, monitoring, maintenance, and raw material/fuel modifications which result in a net decrease in air emissions within the reasonable and practical constraints imposed by capital, operating and energy costs. This section includes discussions of the state-of-the-art of petroleum refinery fugitive and process emission controls; the need for additional controls for some sources; emission control technology used in related industries and its applicability to refining; and the economics of control.

Detailed descriptions of emission sources and control technologies are presented in Appendix E (Volume 4). Emissions from transfer facilities/operations, storage vessels, or other auxiliary processes are not included.

Controls for fugitive emissions are discussed in Section 7.2.1. Included in this discussion are work practice and equipment controls. Equipment controls for process (stack/vent) emissions are described in Section 7.2.2. Section 7.2.3 includes discussions of process, fuel, and feedstock controls for process emissions.

Controls for fugitive emission sources are generally applicable to a particular source type (valve, pump, etc.) and are not unique to any type of process unit. Fugitive emission controls are, therefore, discussed by source type. Process emission controls are discussed on the basis of the type of process unit, because of the differences in emissions and controls between processes.

7.2.1 Control of Fugitive Emissions

In this section the descriptions of fugitive emission control technology are presented for each type of emission source (valve, pump, etc.). The order of presentation is such that sources with similar types of controls are discussed in sequence. The relative contribution of source types for a hypothetical refinery is presented in Section 2.7.3 of Appendix B (Volume 3) of this report.

Three levels of control are described for most sources. Existing controls are those in general refinery use, although the extent of application may be variable. Available control technology may be used in some areas of the refining industry due to regulatory or other requirements. Control technology transfer includes any types of emission controls that have been applied to similar types of emission sources in other industries.

7.2.1.1 Valves

Valves can leak hydrocarbons through the junction where the activating stem penetrates the valve body. Excessive leakage from this junction is generally prevented by a packing gland or a pressurized grease seal. If a valve is operated with one side of the valve seat open to the atmosphere, such as for draining or sampling operations, hydrocarbons may also leak through the valve seat.

Table 7-47 contains the approximate distribution of refinery valves screened by Radian within the battery limits of major process units during the thirteen refinery sampling programs. The distribution of each

TABLE 7-47. APPROXIMATE DISTRIBUTION OF REFINERY PROCESS VALVES[a] BY TYPE AND SERVICE

Type Valve	Valve Type Distribution by Service, %		Total Type Distribution, %
	Manual	Control	
Gate	64.7	0.0	64.7
Globe	3.8	23.3	27.0
Plug	5.7	0.0	5.7
Butterfly	0.6	1.8	2.5
Diaphragm	0.0	0.1	0.1
Total	74.8	25.2	100.0

[a] Check and sample system valves excluded. No dry-service slide valves were surveyed.

type of valve is shown for manually operated and automatically controlled service categories. Approximately 88 percent of all the screened refinery valves were either manual gate valves (65 percent) or control globe valves (23 percent).

Existing Controls for Valves--These controls include the valve stem seal, inspection and maintenance practices, and closure of the atmospheric side of open-ended valves.

Valve Stem Seals--The valve stem seal is designed to prevent leakage of the contained fluid and is therefore a fugitive emission control. All gate, globe, and butterfly valves screened by Radian had a packed gland stem seal. These packed stem valves represent approximately 94 percent of all refinery valves. Plug valves typically have a grease-lubricated, tapered plug to prevent leakage. Grease may be added periodically to prevent leakage and to assure proper operation of the plug valve.

Packed stem seals consist of a stuffing box that surrounds the stem, rings of compliant packing material in the annular space, and a gland or follower that is used to compress the packing against the stem to form a seal. Figure 7-1 is a simplified diagram of the type of packed seal used in valve stems.

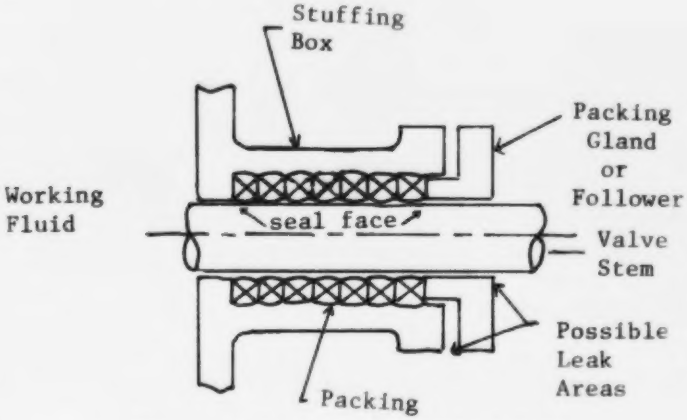

Figure 7-1. Simple Packed Seal

The fluid may be further prevented from diffusing through standard type packing by dispersion of lubricant through the packing. The lubricant also alleviates galling, heating, and scoring of the stem or shaft. In most cases, a lubricant must be compatible with the packing and the working fluid. In refining, this lubricant might be a silicone oil, a petroleum grease, or a TFE or graphite dispersion in an oil or grease.

Lubricants may be present in the coils or rings of packing as received. They may also be introduced into the gland through a "grease" fitting which passes lubricant into the stuffing box.

Table 7-48 shows the diversity of valve packing materials used alone or in combination.[75] Most of these materials may be purchased in coils or in preformed rings. They may be solid or stranded and may have a round, square, "U," or chevron cross-section.

All refineries have operating practices that require repair of any detected leaks. These practices are primarily aimed at preventing fires or other safety hazards that could result from large amounts of hydrocarbon leakage. Visual methods or odor are generally relied upon to detect leaks. However, many leaks from valves and other sources may not be detected by sight, hearing, or smell. It is also a common refinery practice to lubricate valves and tighten packing glands periodically.[76,77]

Open-ended valves may be used for draining, venting, or sampling operations. In addition to fugitive emissions from the stem seal, the valve seat may be a source of fugitive emissions. To prevent emissions through the seat, the open-end can be sealed with a cap, plug, blind flange, or a second valve. Two valves in series (double block and bleed) can also be installed on sampling connection. This provides a second valve seat to resist emissions of the process fluid to the atmosphere.

TABLE 7-48. PACKING MATERIALS - PROCESS VALVES

Packing Material	Form	Use	Temperature
Flexible, all metallic	Spiral wrapping. Thin ribbons of soft babbit foil.	Valve stem packing	Up to 450°F.
Flexible metallic packing (aluminum).	Spiral wrapping. Thin ribbons of soft annealed aluminum foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Flexible metallic packing (copper).	Soft annealed copper foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Long-fiber pure asbestos and fine lubricating graphite (nonmetallic).	Graphite special long-fiber asbestos binder.	Extreme resilience.	Up to 750°F.
Closely braided asbestos yarn; top jacket reinforced with Inconel wire; core: long fiber asbestos.	Spools, die-formed rings.	High-temperature valves.	Up to 1200°F.
Pure asbestos yarn with an Inconel wire insert around a resilient asbestos core impregnated with graphite.	Spool form, die formed.	Valve stem for air, water, steam and mineral oil.	Stuffing box temperature up to 1200°F.
Twisted long fiber Canadian asbestos.	Spool form, die formed.	Valves handling, high and low pressure steam.	Up to 500°F.

(Continued)

TABLE 7-48. (Continued)

Packing Material	Form	Use	Temperature
Asbestos, graphite and oilproof binder.	Spool form, die formed.	Shutoff valves.	Up to 550°F.
Solid, braided TFE.	Coil, spool, ring.	Valve shaft for highly corrosive service.	100°F to 500°F.
Braided asbestos with complete impregnation of TFE.	Coil, spool, ring.	Valve stems in mild chemical or solvent service.	100°F to 600°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite and asbestos.	Coils, spools.	Valve stems, steam, air, mineral oil.	Up to 1200°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite.	Coils, spools.	Stainless-steel valve stems, air, steam, water.	Up to 1200°F.
Braided of long-fiber Canadian asbestos yarn each strand impregnated with heat-resistant lubricant.	Coils, spools.	Valves for steam, air, gas and mild chemicals.	Up to 550°F.
Long-fiber Canadian asbestos yarn, each strand treated with a synthetic oilproof binder and impregnated with dry graphite.	Coils, spools.	Refinery valves.	To 750°F.

(Continued)

TABLE 7-48. (Continued)

Packing Material	Form	Use	Temperature
Braided/overbraided, wire-inserted, white asbestos packing impregnated with a heat-resistant lubricant.	Coils, spools.	Valve stems, for valves handling steam, air, gas, cresylic acid.	Up to 750°F.
Braided white asbestos yarn impregnated with TFE suspensoid.	Coils, spools.	Valve stems.	100°F to 600°F.
Braided or bleached TFE multifilament yarn.	Spools, coils.	Valve stems for highly corrosive liquids.	12°F to 500°F.
Braided TFE multifilament yarn impregnated with TFE suspensoid.	Spools, coils.	Valve stems for corrosive chemicals, solvents, gases.	120°F to 600°F.
Asbestos jacket, braided over a dry-lubricated plastic core of asbestos graphite and elastomers.	Spools and coils.	Valve stems, for valves handling superheated steam, hot gases.	Up to 850°F.

Source: Reference 75.

Effectiveness of Existing Controls--The overall effectiveness of existing controls is reflected in the emission factors given in Section 5 of this report. These emission factors were derived from test data collected from a broad cross-section of thirteen refineries. All levels of the types of control existing at the time of the field sampling (1977-1979) were included. The effectiveness of individual types of existing controls (type of packing, maintenance schedule) could not be determined from the available data.

Available Control Technology for Valves--Leak detection and repair programs are the available controls for valves. Programs of this type are already a regulatory requirement in some areas. They will probably become more common as additional regulatory requirements are promulgated and value of the products lost as fugitive emissions increases.

Leak detection and leak repair programs consist of strategies to identify significant fugitive hydrocarbon emission sources combined with methods to reduce or eliminate the leakage. At a specified interval, each valve would be checked with a portable hydrocarbon detector. If a predetermined hydrocarbon concentration limit (action level) were exceeded, the valve would be repaired. The repair could consist of tightening the packing, injecting grease, replacing the packing, or replacing the valve. During repairs such as tightening or greasing, the hydrocarbon detector should be used to permit assessment of the effect of the repair attempt. This type of repair is called "directed" maintenance.

Effectiveness--In the limited valve repair study conducted by Radian, the average weight percent emission reduction immediately after "directed" maintenance was 91 percent. The detailed results of the maintenance study are shown in Section 6 of Appendix B (Volume 3). They are summarized in Section 5 of this report. Data on the long-term effects of maintenance are not available.

In some cases injection of sealing fluids into the packing area of the valve may be used to reduce fugitive emissions. The effects on emission reduction and valve operability have not been reported. For some control valves, operating procedures may prohibit excessive in-service adjustment to prevent malfunction of vital process control valves.

The required frequency of leak detection is dependent on the rate of recurrence of repaired leaks and the rate of occurrence of new leaks. The selection of an appropriate action level is dependent on the demonstrated ability to repair leaks of a given magnitude. Radian test results indicated that the smaller the initial leak rate, the more likely it is that repair efforts will be ineffective.

Because of the sparseness of data on long-term effectiveness of leak repair, frequency of occurrence of leaks, and the fraction of leaking valves which are unrepairable while in service, no quantitative estimate of the overall emission reduction can be defined.

The major costs for leak detection and repair are for labor expenses. The hydrocarbon detector can cost up to $4,250 per instrument,[78] and if leak surveys were conducted as frequently as once per month each process unit would probably need one instrument. Actual labor costs are dependent on the wage rate of the persons performing the leak survey and leak repairs. Estimates have been made for the time needed to conduct leak surveys. One petroleum refining company has estimated that one minute per valve is the average time required for leak detection.[79] The time needed to repair a leak will be dependent on the type of repair attempted. Simple tightening of packing by refinery employees would obviously be much cheaper than injection of a sealing fluid by leak repair contractors. The total cost of a leak detection and repair program would be reduced by the value of the product that was prevented from leaving the process as an emission. The emission reduction would also represent an energy saving.

Control Technology Transfer for Valves--Fugitive emissions of some process fluids may be hazardous or toxic. In industries with these constraints, valves with isolated stem seals may be used. The diaphragm and bellows-sealed valve are two types of these valves. Because the process fluid is prevented from contacting the stem/body junction by a bellows or diaphragm, the potential for fugitive leakage is reduced. These valves are not generally applicable to refinery use, however, because of several limitations.

The diaphragm material in the diaphragm valve limits operation to about 50 psi pressure differential.[80] This type valve has definite limitations in refinery use. It can fail catastrophically upon overheating of the elastomer diaphragm, so it should not be used in hydrocarbon service where a fire could be fed by its failure. The bellows-sealed valve, because of the corrosion and fatigue failure potential of the bellows, is subject to combined temperature-pressure-corrosivity stress. Its usage is best defined by the valve manufacturer. Bellows-sealed valves should have stem seal packing as back-up protection against bellows failure.

Because use of these special valve stem seals will probably be limited, the impact of their use on emission control should also be limited, as would any economic impact. No primary energy cost would result from substitution of a very limited number of packless valves for conventional packed-stem, bonnet-sealed valves.

Diaphragm and bellows valves are approximately 1.5 to 3.7 times as expensive as gate valves according to the CARB report.[81] Another source estimated that bellows valves might cost 10 to 20 times as much as packed-stem valves, but would have a lower cost multiple if purchased in volume.[82]

7.2.1.2 Flanges

Flanges are paired junctions between sections of pipe and pieces of equipment. They are sealed against leakage by the tightening of bolts or studs which compress a flat gasket between the flat faces of the mating flanges, or compress an "o" ring set in the grooved faces of special flanges. The most common flanges have raised faces to accommodate tightening of the bolt and centering of the gasket. Typical gasket materials are asbestos composition or spiral, metal strip-reinforced asbestos or TFE. "O" rings may be made of neoprene, TFE or soft metals, depending upon temperature and pressure limits.

The results of the refinery sampling program showed that flanges have a very low emission factor, and even though there are many of them, their overall contribution is small. The only real controls available for flanges are leak detection and repair programs. If a leak is found, the only repair options are tightening the flange bolts or injection of a sealing fluid, since most flanges cannot be isolated from the process in order to permit gasket replacement.

A large amount of time would be required to inspect all flanges with hydrocarbon detectors. The expenditure of this time and manpower does not appear justified given the low average emission rate for flanges.

7.2.1.3 Pump Seals

Pump seals prevent the escape of process liquid from the area between the rotating pump shaft and the stationary pump housing. There are two basic types of seals, the packed seal and the mechanical seal. The packed seal can be used on pumps with reciprocating or rotating shaft motion, and mechanical seals are applicable only to rotating shafts.

Existing Control Technology--This study indicated refinery pump-seal combinations fall almost exclusively into one of three broad categories: centrifugal pump - mechanical seal (82.1 percent), centrifugal pump - packed seal (11.5 percent), and reciprocating pump - packed seal (6.4 percent).

The two types of existing controls for pumps are the pump seal itself, and inspection and maintenance of the pump seal. The packed seal and mechanical seal resist leakage of the pumped fluid by different mechanisms, and are described separately.

The packed seal is used to seal both rotary and reciprocating shafts against leakage of liquid from the "working fluid" end of the shafts to the atmosphere. Compressed packing in the stuffing box forms a contact seal against the moving drive shaft. Friction resulting from this contact requires that either the working fluid be allowed to leak from the stuffing box housing the packed shaft, or a supplementary liquid be introduced to remove frictional heat.

Packings for the compression-type packed seals may be solid or braided, twisted or ribbon-form (the latter form in graphite only). They may be obtained in continuous rolls or preformed rings. Packing materials include asbestos/TFE, TFE (lubed), asbestos/graphite, graphite-fiber, graphite-ribbon, lead, aluminum, and Inconel-reinforced asbestos over resilient case.

Under moderate conditions, the trend in braided backings is away from asbestos and toward TFE because of the latter's low coefficient of friction and its chemical inertness.

The mechanical seal in its many forms is the predominant pump seal today. Contrary to the broader application of packed seals to both rotating and reciprocating shafts, however, mechanical seals are used only on rotary shafts. Mechanical seals may be used to seal both pump and compressor shafts, but are more universally applied to pumps, specifically centrifugal pumps.

Mechanical seals are prefabricated assemblies which shift the point of wear from the drive shaft, as with packed seals, to easily replaced pairs of rings. One of the rings is attached to the pump shaft, and the other to the gland plate or its equivalent. Seal faces are perpendicular to the shaft and are typically lapped to a flatness of two light bands. This precise flatness accounts for their typically low leak rate when carefully installed and started up.

Single mechanical seals will generally serve to limit emissions in the majority of applications, but double mechanical seals provide an added margin of protection against seal failure. Double seals normally have a barrier liquid circulating between the seals. If the inner seal should fail, the outer seal will prevent escaping fluid from reaching the atmosphere.

Mechanical seals are used in the majority of refinery pumps. The American Petroleum Institute (API) recommends mechanical seals as particularly advantageous for hydrocarbon emission control in the following cases: (1) ". . .more-or-less continuous pumping of products having a Reid Vapor Pressure of five pounds [per square inch (author's note)] or greater. . ." and (2) ". . .when fluids are under substantial pressure and when the pump or compressor is in continuous service. For pumps operating on stand-by service either packed or mechanical seals may be used."[46]

At the time of the Los Angeles County, California, study twenty years ago, mechanical seals made up only 42 percent of the seals in the use there.[83] In the current refinery study, the percentage was 82 percent. The Radian survey showed this percentage to be further subdivided into approximately 67 percent single mechanical seals and 15 percent double mechanical seals.

Visual inspections are generally used to detect significant pump emissions. In some cases pressure gauges/alarms are used to detect buildup of pressure in barrier fluids of double mechanical seals. Such a pressure buildup indicates failure of the inner seal.

Packed seal emissions can generally be reduced by tightening the packing gland. This can be accomplished while the pump is in service. Emissions from a mechanical seal, however, indicate a mechanical failure in the seal assembly. The pump must be taken out of service, and the mechanical seal can then be replaced.

Frequency of Application, Effectiveness, and Cost of Pump Seals--Application of the types of pump seals is relatively uniform within the refining industry. This may be the result of a greater uniformity of feedstocks and products in the refining industry than in the chemical industry. The application of standards published by the American Petroleum Institute (API) has also undoubtedly led to uniformity among devices used to control fugitive emissions, not only from pumps, but also from some of the other devices tested in this program.

The frequency of application of types of pump seals that was observed in the Radian sampling program is shown in Table 7-49. Sufficient data are not available to compare the relative control effectiveness of the various types of seals.

TABLE 7-49. DISTRIBUTION OF PUMP SEALS IN RADIAN REFINERY STUDY

	Pump Type	Percent of Population
A.	Centrifugal Pump - Mechanical Seal	82.1
B.	Centrifugal Pump - Packed seal	11.5
C.	Reciprocating Pump - Packed Seal	6.4
	TOTAL	100.0

Table 7-50 presents a cost breakdown of pump system elements for systems rated at 3 - 200 horsepower. May, 1980 costs were rolled back to mid-1979. Cost estimates of packed and mechanical seals are shown in part (5) of the table in mid-1979 dollars, and in part (6) as percentage add-on costs to bare, uninstalled pump costs [Subtotal (4)]. These add-on costs for seals range from 1.2 to 3.0 percent for packed seals to 14.2 to 36.4 percent for double mechanical seals for the most common shaft size of 1.375 inches diameter.

Table 7-51 contains a comparison of seal friction losses and hydrocarbon leak estimates for packed seals and three basic types of mechanical seals. Friction losses and hydrocarbon losses are known to vary widely with the fluid properties of the sealed liquid, the seal face materials, the condition of the seal, bearings and shaft, and seal design, so these figures are presented only as approximations of expected performance.

Inspection and Maintenance--All refineries practice inspection and maintenance of pump seals to prevent fire hazards resulting from complete seal failure. Pump seals are usually inspected visually once per day or per shift. Packed seals can be adjusted while in service to reduce leakage, but mechanical seals usually require removal for repair.

TABLE 7-50. CENTRIFUGAL PUMP SEALS - COST CONTRIBUTION TO TOTAL PUMP COST*

	Pump Horsepower Shaft Diameter, Inches	3.0 1.875	100. 1.875	100. 2.375	200. 2.375
1.	Pump, including shaft, coupling, bore plate, seal/bush hardware as required. (Installation costs not included)[a]	2830	4670	4810	6370
2.	Switchgear - Switch, enclosure lighted push botton.[b]	620	1940	1940	4110
3.	Driver - Electric[c]	230	2850	2850	8750
4.	Subtotal	3680	9460	9600	19230
5.	Seal Alternatives				
	a. Packed Seal[d]	110	110	130	130
	b. Single Mechanical Seal[e]	860	860	1000	1000
	c. Double Mechanical Seal[f]	1340	1340	--	--
6.	Seal Costs - Percentage of Subtotal (4)				
	a. Packed Seal	3.0	1.2	1.4	0.68
	b. Single Mechanical Seal	23.4	9.1	10.4	5.2
	c. Double Mechanical Seal	36.4	14.2	--	--

*Mid-1979 Costs = May, 1980 Dollars x 0.921

Bases:

[a] Reference 84. Pump built to API Specification 610,[85] and upon the following conditions:
1) Low corrosion--steel pump casing, cast iron/steel impeller
2) Seal gland pressure--200 psig (~1/3 of discharge pressure maximum)
3) Pumped Fluid--light gasoline
4) Pumped Fluid Temperature-- ≤ 350°F
5) Shaft Speed--3500 RPM

[b] Reference 86. Switch gear--explosion-proof, locally-mounted push button stop-start with red light for "ON" indication.

[c] Reference 84. Electric Driver--Three phase, 400 volt, explosion proof.

[d] Reference 87. Packed Seal--Cost of packing materials approximate.

[e] Reference 88. Single Mechanical Seal--Crane Packing Co. #8-B-1 with throttle bushing as back-up.

[f] Reference 87. Double Mechanical Seal--Chesterton Seal No. 241.

TABLE 7-51. ESTIMATED ENERGY LOSSES - PUMP SEALS

Seal Type	Seal Power Consumption, kW[a]	Hydrocarbon Leak Estimates, lb/hr Open Literature	Hydrocarbon Leak Estimates, lb/hr This Study[b]
Packed	1.16	0.264[c]	
Single mechanical, unbalanced	0.422	$\geq$0.0044[e]	0.16-0.37,[d] all pumps
Single mechanical, balanced	0.194	$\geq$0.0044[e]	
Double mechanical, balanced	0.287	$\cong$0.00[f]	

[a] Reference 89.

[b] See Appendix B (Volume 3), p. 2-263, pumps, light liquids.

[c] Based upon 60 drops/min of hexane @ 20 drops/mℓ. Reference 90.

[d] Range based upon 95% confidence interval.

[e] Based upon as little as 1 drop/min. of hexane @ 20 drops/mℓ. Reference 91.

[f] Reference 91.

Bases: Pump shaft dia.--1.875 in.; stuffing box pressure--200 psig; barrier fluid pressure--175 psig (double mechanical seal only); pump speed--3500 rpm; pump horsepower range (typical)--3-100 h.p.

The effectiveness of these inspection and maintenance programs is reflected in the emission factors presented in Section 5 of this report.

Available Control Technology for Pumps--Leak detection and repair strategies are the available controls for pumps. The procedures for finding leaks requiring repair are the same as those described previously for valves.

No data are available to quantify the effectiveness or cost of leak detection and repair for pumps. Effectiveness would be dependent on initial leak rates, the ability to repair the leaks, and the length of time before the leaks reoccurred. Costs would be dependent on labor rates, labor requirements, and the value of the product saved. Average leak detection time required for pumps has been estimated to be five minutes per seal, and the average leak repair time has been estimated to be 80 hours per seal.[81]

Technology Transfer for Pumps--Sealless pumps are used in other industries in cases where the pumped fluid is toxic or otherwise hazardous and leakage cannot be tolerated. Sealless pumps include diaphragm pumps, hermetically sealed "canned" pumps, and magnetically coupled pumps. Since these pumps do not have a shaft/casing seal, their emission potential is much lower. Emissions may result from diaphragm failure or case failure.

Sealless pumps are not covered by API Standard 610[85] for pumps, which may explain why no sealless pumps were found in the 13 refinery survey. If sealless pumps are to be used in the refining industry, they must be proven performers in terms of leak-tightness, reliability, maintainability, useful life and safety.

The original cost of a "canned" pump may be approximately 110 to 115 percent of the cost of a centrifugal pump with conventional seals.[92] No data are available to discern differences among the other true costs of running conventionally-sealed versus sealless pumps. Sealless pumps also have a more limited range of applicability due to limitations on temperature, throughput, and horsepower.

7.2.1.4 Compressor Seals

A number of types of compressor seals reduce emissions of the compressed gas from the compressor housing. The five basic types are packed (reciprocating shaft), labyrinth (rotating shaft), restrictive ring (rotating shaft), liquid film/bushing (rotating shaft), and mechanical contact (rotating shaft).

The basic principle of packed compressor seals is similar to packed pump seals. However, cooling of friction-type compressor seals differs from cooling of pump seals of similar construction in that the gaseous compressor working fluid provides negligible lubrication and has a lower heat capacity than does liquid. For these reasons most, but not all, contact-type compressor seals use some form of liquid seal coolant which may also serve to reduce gas emissions.

The various types of nonpacked seals differ substantially from each other and from mechanical pump seals. Both the packed and mechanical types of compressor seals are described in detail in Appendix E (Volume 4).

Existing Control Technology--The five basic types of compressor seals are applied in refinery service. The API has estimated that 60 - 70 percent of refinery compressors have packed seals, 10 percent have mechanical contact seals, and about five percent have labyrinth seals.[93,94]

Radian found that approximately 80 percent of the compressors surveyed in the current study had reciprocating shafts with packed seals. About 60 percent of the compressors process gas which contains less than

50 percent hydrogen. The remaining 40 percent compress streams which are predominantly hydrogen.

The various types of compressor seals cannot be universally applied in any or all refinery operations. Because of lubrication and cooling limitations, packed seals are rarely used around rotating shafts. The labyrinth seal allows some gas to continually escape. Nelson[95] states that the loss rate or recycle rate from this type of seal is not generally acceptable today for energy and environmental reasons. For this reason, labyrinths are now more often seen in outboard seals in combination with other sealing devices.

The restrictive ring seal is superior to the labyrinth seal alone, but is limited to about 200 psi and relatively clean gas service.[93,95] Sealing and scavenging ports may be used for labyrinth seals and for restrictive ring seals.

The liquid-film seal is relatively simple, and is not subject to significant wear. It is capable of operating at pressures of up to 5,000 psi in a multiple seal configuration, but has, in all configurations, a relatively complicated piping and control system.[95]

The mechanical contact seal differs significantly from a mechanical pump seal, but utilizes the identical concept of zero clearance at closely-lapped wear surfaces to limit leakage. This type of seal is limited to pressures of about 500 psi. Its leak rate is the lowest for the seals described, but, like mechanical seals for pumps, mechanical contact seals are subject to catastrophic failure. Their oil supply systems, where used, are simpler than oil supply systems for liquid-film seals.[95] Mechanical contact seals form a nearly perfect seal when at rest[95] in contrast to pump mechanical seals which are believed to seal better when the faces are rotating.[7]

Many compressors have enclosed seal areas which are vented to the atmosphere from "high-point" vents for safety reasons. Compressors are often housed in semi-enclosed or completely enclosed buildings. Many handle gases which contain toxic or hazardous components such as hydrogen sulfide. Venting the seal area to a high-point vent reduces the potential for a buildup of toxic or explosive gases in the compressor area.

Sealant or lubricating oil is circulated through and around compressor seal mechanisms. This oil is under pressure and will contain the components of the compressed gas. The oil must be depressured and/or treated to remove these gases. The vapor from the degassing of the seal oil is generally vented to a blowdown/flare system.

Gases from the seal enclosures or seal oil degassing are sometimes drawn off by vacuum educators and sent to flare/blowdown systems.

Effectiveness of Compressor Seals--Table 7-52 shows a comparison of seal leakage. The worst, the straight pass labyrinth, is given a gas leakage index of 100. It is not clear from the table, which includes both dry and lubricated seals, where the oil film seal fits in according to the gas leakage index. The liquid film seal is shown, however, to lose more lubricant than the lubricated mechanical contact seal by a factor of 55. It is not clear if this refers to oil loss into the compressed gas stream or if it refers to loss of oil (and dissolved gas) to the atmosphere.

The packed seal is the only seal available for a reciprocating compressor application. The mechanical contact seal, wet or dry depending upon design needs, would appear to rank the best among centrifugal compressor seals for pressures up to about 500 psi. However, these seals are said to be fragile and prone to failure, as well as complex and difficult to install correctly.

TABLE 7-52. COMPRESSOR SEAL LEAKAGE

Compressor Seal	
Dry Types	Gas Leakage Index
Straight Pass Labyrinth	100
Staggered Labyrinth	56
Honeycomb Labyrinth	40
Restrictive Ring	20
Mechanical Contact (Running Dry)	2
Oil Types	Oil Loss
Mechanical Contact $6\frac{3}{4}$ in. Face Diameter 30 psi Differential 500 rpm	0.03 gal/hr
	Lubricant Loss
Liquid Film or Bushing $5\frac{1}{2}$ in. Bore Diameter 0.007 in. Clearance 5000 rpm 60°F Oil Rise	1.75 gal/hr or 55 times the contact type

Source: Reference 95.

A more flexible device in terms of broad pressure range application (to 5,000 psi) and suitability for dirty gas service is the liquid film seal. The complexity of its external circulation and control system would be perhaps its most costly feature. Acid gas stripping from circulating seal oil is a must with the use of liquid film seals if the working gas is sour. The oil reservoir degassing vent may be a source of hydrocarbon emissions.

Seal Energy Requirements and Cost--Compressor seal design is traditionally an integral part of overall compressor design. As a result, data are not available to allow independent seal energy usage and cost analysis.

Inspection and Maintenance--Existing inspection and maintenance procedures for compressors are similar to those described for pumps. Leakage may be more difficult to detect because some compressors have enclosed seal areas that transport leakage to an elevated vent pipe. The effectiveness of these procedures is reflected in the emission factors for compressors shown in Section 5 of this report.

Available Controls for Compressors--Closed vent systems and leak detection and repair programs are the available controls for compressors. A closed vent system consists of piping and, if necessary, flow inducing devices that transport compressor seal leakage to a control device. Control devices could include fired heaters or boilers, incinerators, flares, or vapor recovery systems. For compressors with seal oil systems, the closed vent system can be connected to the seal oil reservoir degassing unit. For other compressor seals, the seal area itself could be enclosed and connected to the closed vent system.

Leak detection and repair for compressors is similar to the program described for pumps. A hydrocarbon detector can be used to detect seal leaks. These areas would include the seal itself (if accessible), the seal vent pipe, and the seal oil reservoir vent depending on the physical configuration of the compressor. No data are available to quantify effectiveness of the leak detection and repair for compressors. Effectiveness and cost would be dependent on the same factors discussed for pumps. Average leak detection time required for compressors has been estimated as 10 minutes per seal, and repair time has been estimated as 40 hours per seal.[81] One major difference between repair of pump and compressor seals is that most refinery pumps have spares, but many compressors do not. Therefore, any repair that required compressor shutdown might also require shutdown of the process unit. Depending on the type of process unit, the unit shutdown could cause more emissions than allowing the compressor seal to leak until repair can be effected during the next turnaround or shutdown.

Technology Transfer for Compressors--No other controls were identified for compressor seal leakage. Sealless compressors are not available in the capacity range that would be required in almost any refinery application.

7.2.1.5 Agitators

Agitators may leak hydrocarbons at the junction of the vessel and the rotating agitator shaft. The agitator seal may be in liquid service if the agitator is located at the side of a storage tank, or the seal may be in vapor service if the agitator is located at the top of reactor vessels. In some types of refinery operations, in-line blending has replaced the use of agitated mixing vessels.

Existing Controls for Agitators--The four basic types of agitator seals are listed in Table 7-53. Some of the seals are similar to pump seals (packed and mechanical). The limitations of the four seal types are shown in Table 7-53. No data are available to establish the magnitude of leakage from agitator seals. The seals are listed in Table 7-53 in order of increasing cost.

TABLE 7-53. BASIC AGITATOR SEALS

Seal Type	Limitations	Comments
a. Hydraulic	Low pressure and temperature	Least-used agitator seal.
b. Lip	2-3 psi; unlubricated	Dust or vapor seal only; temperature limited by elastomer lip melting point.
c. Packing Gland	150 psi	Six packing rings and lantern ring required for 150 psi capability.
d. Mechanical Face	0 psia to 5,000 psia if housed and pressured to working fluid pressure	Externally lubricated so as to leak in if inboard seal fails (double seal configuration). Single seals also used.

Source: Reference 96.

Available Controls for Agitators--Leak detection and repair strategies for agitators should be similar to those described for pumps and compressors. The time required to detect leaks is probably about the same as for pumps and compressors. The time requirements for repair are not quantified.

7.2.1.6 Safety Relief Valves

Safety relief valves (SRV) are installed on any refinery equipment that could be subjected to overpressuring with subsequent safety hazards and equipment damage. The various types of SRV's in hydrocarbon service are described in detail in Appendix E (Volume 4). Emissions to the atmosphere occur through the valve seat due to improper seating, which can be a result of wear, corrosion, or foreign matter.

Existing Controls for Safety Relief Valves--Inspection and maintenance is one existing control for SRV's. The main objective of most inspection and maintenance programs is to make sure the SRV will provide proper over-pressure protection. Some companies remove and test SRV's after every over-pressure release.[81] This procedure requires that a means be provided to install a spare SRV while the other one is tested. Although this testing is primarily to check the set pressure of the SRV, it may also detect fugitive leakage. The other existing control for SRV's is discharge header systems that transport over-pressure releases (and fugitive leakage) to a flare.

Available Controls for Pressure Relief Devices--Leak detection and repair programs and upstream rupture disks are the available controls for SRV's. Leak detection would require periodic testing of SRV's that discharge to the atmosphere. A hydrocarbon detector can be used to detect hydrocarbon concentrations at the exit of the discharge "horn" or at the weep hole at the bottom of the "horn." Repair of the SRV would probably require removal of the SRV, and therefore a means of replacing the SRV while the process unit was operating would be needed. Data on costs and effectiveness of leak detection and repair for SRV's are not available.

Although most SRV's are used alone or in pressure-stepped combinations, some are used with rupture disks mounted under them (i.e., between the process fluid and the SRV). Rupture disks (RD's) are somewhat prone to age-induced fatigue or corrosion failure, and therefore are not ordinarily used alone except where complete loss of process fluid is acceptable economically and environmentally. Such acceptable cases probably no longer exist in any organic chemicals or fuels manufacturing facility.

Alternatively, rupture disks may be positioned downstream of SRV's to protect working parts from weather or other corrosive atmosphere, as when connected to a relief header.

Rupture disk leaks may be detected by "tell-tale" bubblers or pressure gauges, and by excess flow valves connected to the inside piping space between the RD and the SRV. This arrangement is covered by ASME code.[97] If small RD leaks are not monitored, there is a chance that the pressure between the RD and SRV might build to system pressure. Then, with a rapid rise in pressure, as in an emergency, working pressure would almost double before the disk and SRV would release, depending upon the rate of increase and size of the RD leak.

As long as the integrity of the rupture disk is maintained, fugitive emissions are completely eliminated. The disk would require replacement after over-pressure release, and therefore a means for replacing it while the process unit was in service would be needed. Although there is controversy within the industry concerning the use of rupture disk-safety relief valve combinations, some feel that the combination may be operated safely.[97] Others consider RD use upstream or downstream of the SRV only as necessary for either (1) added isolation of particularly toxic materials from the air, or (2) as a means of isolating the SRV from a corrosive atmosphere. This atmosphere might be, for example, a header with sulfur compounds present, or simply salt air near the ocean.[98]

Costs--The addition of an inlet or outlet side rupture disk to an SRV adds between three percent and 50 percent to the materials cost of the SRV, depending on size and service. Materials costs for SRV and RD assemblies (excluding piping) are shown in Table 7-54. The net cost of the system would take into account a value for the product saved by eliminating fugitive emissions.

Technology Transfer for Pressure Relief Devices--Fugitive leakage caused by improper reseating after over-pressure release may be minimized by using pilot operated SRV's with resilient (O-ring) seats. No data are available to quantify the effectiveness of this type of control. Another potential improvement in SRV design would be to install parallel SRV's in all applications. This would allow an SRV to be in service with the other blocked off as a spare. The SRV could then be removed for testing and rupture disk replacement after over-pressure releases.

7.2.1.7 Sampling Connections

Fugitive emissions from sampling connections are primarily due to purging the sample line to obtain a representative sample. Atmospheric exposure of the purged fluid can result in evaporative hydrocarbon emissions.

Existing Controls for Sampling Connections--Existing practices for obtaining process samples vary considerably. They may range from draining process fluid onto the ground to collection of the purge in slop oil systems. All existing practices result in some atmospheric exposure and emissions, but the magnitude has not been quantified.

TABLE 7-54. SAFETY RELIEF VALVE (SRV) AND RUPTURE DISK (RD) ASSEMBLY COSTS

System Size, Inlet × Outlet diameter, inches	May 1980 Dollars			
	SRV		RD Assembly	
	150 psi flanges	300 psi flanges	Inlet	Outlet
1 × 2	650	700	320	120
3 × 4	1,050	1,150	520	160
8 × 10	5,900	7,800	1,100	220[a]

Basis: Materials only; piping excluded. May, 1980 prices.
RD assembly includes cost of safety head and one disk.

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[a] Interpolated from 4 inch and 12 inch diameter RD costs.

Source: Reference 99.

Available Controls for Sampling Connections--Closed loop sampling systems are the primary control available to reduce sample purge emissions. A closed loop sampling system consists of a network of piping and valves that either returns the purged material directly to the process, or that transports the purge to a closed collection system for recycle.

Technology Transfer for Sampling Connections--The main innovations that are likely to reduce sample purge emissions are the increasing availability of on-line continuous analytical instruments that do not require discrete samples.

7.2.1.8 Wastewater Systems

Refinery wastewater systems have evolved over the years as awareness of water pollution problems has grown, and as various treatment systems have been developed. There are four basic treatment steps.[100] The first is primary separation, where oil is removed by gravity separation. Normally, an API or a CPI-type separator is used. These separators effectively remove free oil from water, but will not separate substances in solution or break up emulsions.[101] The second step is intermediate separation where suspended solids and additional oil are removed by chemical sedimentation or air flotation. Secondary treatment is the third step. It involved the reduction of the biological oxygen demand (BOD) with some type of biochemical oxidation. Finally, in the tertiary treatment step, dissolved organics which will not degrade with biological treatment methods are removed. Carbon adsorption is the most common form of tertiary treatment.

The treatment processes for these steps are shown below.[102]

- Primary--API Separators, Tilted-Plate Separators (CPI), Filtration for Oil Removal, pH control, and Stripping Processes.

- Intermediate--Dissolved Air Flotation, Coagulation-Precipitation, and Equalization.

- Secondary-Tertiary--Carbon Adsorption, Activated Sludge, Aerated Lagoons, Trickling Filters, Waste Stabilization Ponds, Cooling Tower Oxidation, Chemical Oxidation, and Filtration.

In addition, there is a wastewater collection system which consists of process drains, sewers, holding basin, and pumps.

Existing Controls for Wastewater Systems--Table 7-55 gives an estimate of the degree of adoption of various wastewater treatment processes for 1950, 1963, 1967, 1972, and 1977. While this table utilizes the author's judgment in many areas due to the "dearth of usable information," the data on API separators are reliable and confirm that by 1977 nearly all refineries had an oil and water separator of the API or the CPI type.[103] The table also shows an increasing use of intermediate, secondary and tertiary treatment methods. This trend is a result, in part, of governmental scrutiny and control in the area of water pollution.

Covered oil/water separators and trapped drain systems are two types of emission controls used in some refineries. Some state regulations require covers for separators. As of January 1977, 80 percent of the U.S. refining capacity was located in states where covers are required.[104] The extent of application of trapped drain systems is not known. Because of the lack of emission data, effectiveness of those controls cannot be assessed. Costs would vary widely, depending on site specific conditions.

The current AP-42 emission factors for drains and oil/water separators, uncovered versus covered, imply a 95 percent fugitive hydrocarbon emission reduction. The original data upon which the AP-42 emissions are based are no longer available.[105] Thus, the validity of the

TABLE 7-55. DEGREE OF ADOPTION OF VARIOUS WASTEWATER TREATMENT PROCESSES

Processes and Subprocesses	Percent of Refineries Using the Processes				
	1950	1963	1967	1972	1977
API Separators	40	50	60	70	80
Earthen Basin Separators	60	50	40	30	20
Evaporation	0-1	0-1	1	1-2	2-5
Air Flotation	0-1	10	15	18	20
Neutralization (Total Wastewater)	0-1	0-1	0-1	0-1	0-1
Chemical Coagulation and Precipitation	1-5	1-5	5-10	10-15	10-15
Activated Sludge	0	5	10	40	55
Aerated Lagoons	0	5	10	25	30
Trickling Filters	1-2	7	10	10	10
Oxidation Ponds	10	25	25	25	20
Activated Carbon	0	0.5	0.5	3	5
Ozonation	0	1	1	3	5
Ballast Water Treatment - Physical	9	9	8	5	5
Ballast Water Treatment - Chemical	1	1	2	5	5
Slop Oil - Vacuum Filtration	0	5	7	12	15
Slop Oil - Centrifugation	0	2	3	10	15
Slop Oil - Separation	100	93	90	80	70
Sour Water - Steam Stripping - Flue Gas Strippers - Natural Gas	60	70	85	90	90
Sour Water - Air Oxidation	0	3	3-5	7	10
Sour Water - Vaporization	1	1-2	1	0	0
Sour Water - Incineration[a]	35-40	40	50	30	20
Neutralization of Spent Caustics					
Flue Gas	20	30	35	20	20
Spent Acid (including springing and stripping)	15	25	30	25	20
Oxidation	0	3	5	5	5
Incineration	25	40	50	20	15

[a] Incineration includes flaring, boiler furnaces, and separate incinerators used only in conjunction with stripping and vaporization.

Source: Reference 103.

indicated effectiveness cannot be assessed. In a laboratory study using a simulated API separator, the covered separator provided 89 percent emission reduction.[106]

The data from Radian's oil-water separator emission measurements are discussed in Appendix B (Volume 3). The results are poor and cannot be used to develop emission factors for oil-water separators.

It is evident that further study of evaporative losses from oil-water separators is needed and justified. Actual emission rates for uncovered separators probably fall between 13 and 200 lb/1,000 bbl refinery feed. Similarly, average losses from covered separators can be expected to be between 1.5 and 20 lb/1,000 bbl refinery feed.

Available Controls for the Wastewater System--In general, available controls for reducing fugitive emissions from existing process and storm sewers and collection systems consist of minor modifications such as sealing open sewer systems, altering pump bases, recurbing some process areas, and improving housekeeping.

Changes which involve substantial capital outlays (or which may be nearly infeasible from a construction standpoint), such as major revisions to existing underground sewer systems or installation of vapor recovery systems may not be practical. Techniques which can be used to reduce emissions from the collection system are listed below.

- Open drains, sewers, or holding basins (which regularly receive water containing significant quantities of volatile organic compounds) upstream of the oil and water separator should be eliminated where practical. These sources of emissions in the U.S. refining industry are now fairly rare. The evaporation of significant volumes of oil at current world scale prices is a readily apparent financial burden. Process drains and sewers should be covered or vented through liquid seals wherever safe and practical.

- Pump bases which do not drain completely by gravity should be altered. Many pump bases are designed so that a slight level of oil (from a leaking seal) must build up before the base drains to the sewer. When new pumps are to be installed, bases should be selected which allow proper drainage. Existing pump bases can be modified.

- Segregation of process water from storm water and minimization of oily water volumes should be practiced wherever practical. Curbing should be installed so that only those areas which are subject to oil spills drain into the oily water sewer system. Storm sewers should be sized so that overflow into process sewers during peak runoff is avoided. In many cases, however, substantial revisions to the sewer systems of older plants can be very expensive.

- General housekeeping can be improved. An undefined but, in some cases, significant source of emissions is the lack of good housekeeping practices concerning oil spills and leaks. A quantitative control technique in the area of oil spills and leaks could probably not be formulated, but an awareness of the problem would be beneficial.

Adequate data are not available for a definitive evaluation of the effectiveness of covers on oil-water separators for reducing atmospheric emissions. It seems reasonable to presume that covers will reduce emissions to some degree. The cost-effectiveness of this control option can only be determined after its control efficiency has been defined through testing. There can be safety and operational problems associated with covering the separators. These must be evaluated on an individual basis.

API separators can be covered by a number of methods including floating pontoons or double-deck-type covers which are sealed against the outer walls of each bay. A CPI separator normally has a fixed roof cover.[104]

Cost of Controls--The cost of installing covers on API separators can be substantial. The area of required coverage has been variously estimated at 0.028 ft^2 per bpd wastewater flow and at 0.050 ft^2 per bpd crude oil to the refinery.[104,107] These same sources have cited costs for covers of \$14.40/ft^2 (mid-1978) and \$12.50/ft^2 (mid-1977), respectively. These costs can be escalated to current prices by using the M&S equipment cost index reported in Chemical Engineering.[108] The current cost of covers then becomes \$15.84/ft^2 and \$14.85/ft^2, respectively. If a cost of \$16.00/ft^2 and a cover size of 0.050 ft^2/bpd crude oil charge are used, the capital cost alone is \$265,000 for covers for the 330,000 bpd hypothetical refinery.

7.2.1.9 Cooling Towers

Hydrocarbons can be found at very low levels in nearly all water used for refinery process cooling. If significant leaks occur in process heat exchanges, the level of hydrocarbons present in the circulating cooling water can increase substantially. Some of these hydrocarbons can be vaporized and emitted to the atmosphere in the cooling tower.

Existing Control Technology--Existing controls of hydrocarbon emissions from cooling towers consist primarily of heat exchanger inspection and maintenance. These practices minimize the leakage of hydrocarbons into the cooling water. Monitoring for total organic carbon (TOC) in cooling water is commonly practiced in refineries. This procedure detects small increases in the hydrocarbon concentration and provides an early indication of small leaks. These leaks can often be found and repaired before they become large and while the air emissions are still small.

Emission factors determined during this study were based on two analytical methods: Total Organic Carbon (TOC) analysis and a purging technique. These emission factors are shown in Table 7-56. The emission factor for uncontrolled cooling tower emissions currently included in AP-42[7] is 6 lb/10^6 gallon of circulating cooling water. In Radian's study of cooling tower emissions, the purge method of analysis was found to be much more precise than the TOC technique. Therefore, the emission factor of 0.11 lb. nonmethane hydrocarbons per 10^6 gallon cooling water is recommended for controlled emission.

TABLE 7-56. RADIAN-GENERATED COOLING TOWER EMISSION FACTORS

Analytical Technique	Emission Factor, lb HC/10^6 gal C.W.
TOC	12.4
Purge	0.11

Available Controls for Cooling Towers--The best control for cooling towers is to minimize the amount of hydrocarbons entering the tower. One method to achieve this goal is to eliminate the use of contaminated process water as cooling tower make-up. This may be difficult, since efforts to reduce water discharges may require the use of process water for cooling towers. Another control option is to monitor the hydrocarbon content of the cooling tower input. If elevated concentrations are detected, a leak in the process equipment is indicated. The problem then is to identify the specific leak and to repair it.

7.2.1.10 Solid Waste System Alternatives

Petroleum refineries generate numerous solid waste streams. These streams may contain many substances, including volatile hydrocarbons. Nonmethane hydrocarbons may be emitted to the air during disposal operations.

Most solid wastes are residuals from wastewater treatment. The exceptions to this are some spent catalysts which are recovered in segregated containers, spent acids and caustic, and other spills and sediments which can be segregated. Normally these exceptions are handled separately from other solid wastes.

The five general categories of solid waste disposal alternatives are landfarming, incineration (with landfilling of the ash), landfilling, deep-well injection, solidification (producing relatively inert substances which chemically or physically isolate the pollutant), or surrounding the pollutant by encapsulation.[109] Landfarming, incineration, and landfilling, which are the most common methods of disposal for refinery solid wastes, can create emissions to the atmosphere.

Existing Controls and Their Effectiveness--There are no specifically recommended emission control technologies for application in landfarming and landfilling. The disposal problems are individualized and depend on the type of solid waste, the solids content, and the properties of the earth at the disposal sites. In general, solid wastes in landfills should be dewatered and/or contained if necessary, and covered with a quantity of earth sufficient to minimize vapor loss and odor problems. Landfarmed materials should be covered or plowed into the earth as soon as possible after application. The solid waste loading capacity of the particular disposal areas should not be exceeded.

A number of types of incineration systems, including multiple-hearth and fluidized bed systems, are available to burn refinery sludges. Control devices will generally be required to reduce particulate emissions from incinerators. Effective particulate controls are venturi scrubbers, impingement scrubbers, bag filters and ESP's, but these devices are much more expensive than scrubbers.

Landfarming and landfilling are economically attractive alternatives to incineration.

7.2.2 Control of Stack and Other Process Emissions

In general, the major sources of atmospheric process emissions are sulfur recovery, fluid catalytic cracking catalyst regeneration, and process heaters/boilers. Other sources include vacuum distillation, coking, air blowing, chemical sweetening, acid treating, blowdown systems, and compressor engine exhaust.

7.2.2.1 Sulfur Recovery

Any crude oil with more than 0.5 weight percent sulfur is generally considered sour and its products are subjected to sulfur removal processing.[51] If not removed, the sulfur can cause corrosion, pollution, and catalysis problems during refining or when the products are used as fuel or as petrochemical feedstocks.

Sulfur removal from whole crude is not generally economical.[110] Various intermediate stock streams are, however, routinely subjected to sulfur removal. The sulfur components in these streams are converted to hydrogen sulfide by contact with hydrogen over a nickel-molybdenum catalyst at an elevated temperature. The resulting H_2S may be removed from the stream and concentrated by one of several means, the most common of which is absorption.

At one time this H_2S was simply burned with other light gases as refinery fuel. In recent years, to minimize SO_x emissions and to produce elemental sulfur for sale to other industries, the Claus process has been used. The tail gas from a Claus unit is the main source of SO_x emissions in a refinery today; it contains H_2S, SO_2, CS_2, COS, S_x, and also CO formed from small amounts of hydrocarbons and CO_2 in the feed stream.

The Claus Process--Because of its economic advantages, a Claus unit for the conversion of H_2S to elemental sulfur is often considered as simply part of normal refining operations. However, because the process by itself is not totally efficient in producing elemental sulfur, the tail gas from the unit can be a major source of emissions. But it must be recognized as a very effective control device.

The Claus process works best for gas streams containing greater than 20 volume percent H_2S and less than 5 volume percent hydrocarbons.[51] There are several flow schemes available according to the H_2S content of the feed stream to the unit. In any case, the overall Claus reaction is as follows:

$$H_2S + \frac{1}{2} O_2 \rightleftharpoons \frac{1}{n} S_n + H_2O \qquad ,$$

where n represents the various molecular forms of sulfur vapor.

CS_2 and COS are produced in side reactions, and usually pass unchanged to the tail gas. They can account for 0.25 to 2.5 percent of the sulfur content of the tail gas.[111] However, with proper design, including the use of the cobalt molybdenum catalyst and a higher inlet temperature in the first reactor, the CS_2 and the COS concentrations in the tail gas can be minimized.[112]

A Claus unit with one catalytic reactor can convert 80 to 86 percent of the H_2S to elemental sulfur.[51,113] This efficiency can be greatly enhanced by repeating the catalytic stage one or more times. Conversion is ultimately limited by the reverse reaction. Recovery rates for various feed compositions are given in Table 7-57.

These efficiencies, once considered sufficient, do not meet new regulations. Further treatment of the Claus unit tail gas is required.

Claus plant costs are sensitive to the flow rate and composition of the input stream as well as the sulfur removal efficiency. It is difficult to generalize the costs. As an example, however, the capital investment costs for a Claus plant having a capacity of 250×10^6 ft^3/day of gas are \$$14 \times 10^6$ (construction period is 4th quarter 1979 through 4th quarter 1980). This plant has a sulfur removal efficiency of about 95 percent.

Existing Control Technology for Sulfur Recovery--The tail gas from the Claus unit is often incinerated before it passes to the atmosphere. Some tail gas treating processes require that the tail gas be incinerated prior to treatment.

More than 70 methods have been proposed for treatment of the Claus unit tail gas.[114] These methods may be continuations of the Claus reaction or add-on processes with chemistry quite different from that of the Claus reaction. The six tail gas clean-up methods listed in Table 7-58 are those considered the most viable at present in light of energy demands, economics, and effectiveness. Amoco's CBA Process, the Sulfreen Process, and the IFP Process are continuations of the Claus reaction under

TABLE 7-57. TYPICAL COMPOSITIONS OF FEED STREAM AND TAIL GAS FOR A 94 PERCENT EFFICIENT CLAUS UNIT

Component	Sour Gas Feed Volume %	Claus Tail Gas Volume %
H_2S	89.9	0.85
SO_2	0.0	0.42[b]
S_8 vapor	0.0	0.10 as S_1
S_8 aerosol	0.0	0.30 as S_1
COS	0.0	0.05
CS_2	0.0	0.05
CO	0.0	0.22
CO_2	4.6	2.37
O_2	0.0	0.00
N_2	0.0	61.04
H_2	0.0	1.60
H_2O	5.5	33.00
H.C.	0.0	0.00
	100.0	100.00
Temperature, °F	104	284
Pressure, psig	6.6	1.5
Total Gas Volume[a]	--	3.0 × feed gas volume

[a] Gas volumes compared at standard conditions.

[b] NSPS requires an emission of less than 250 ppmv (0.025%) SO_2, zero percent O_2, dry basis if Claus Unit Tail Gas is oxidized as the last control step, or, 300 ppmv SO_2 equivalent reduced compounds (H_2S, COS, CS_2) and only 10 ppm H_2S as SO_2, zero percent O_2, dry basis, if the Tail Gas is reduced as the last control step.

Source: Reference 48.

TABLE 7-58. EXISTING METHODS FOR REMOVAL OF SULFUR FROM CLAUS TAIL GAS

Name	Developer	Description	Final Tail Gas S Concentration	Product	Cost (% Cost of Claus)
CBA	Amoco	Claus reaction continued at low temperature; removal of condensed sulfur drives reaction. Bed regenerated with hot gas from Claus unit.	1500 ppmv S	S_0	50-150%
Sulfreen	SNPA/Lurgi	Claus reaction continued at low temperature as in CBA. Bed regenerated with hot nitrogen.	1500-2000 ppm S	S_0	50-150%
IFP-1500	Institut Francais du Petrole	Claus reaction occurs in a solvent.	1000-2000 ppm S	S_0	variable
BSRP	Ralph M. Parsons & Union Oil Co. of California	All sulfur compounds reduced to H_2S which is processed in a Stretford unit.	250 ppm S or less	S_0	100%
SCOT	Shell	All sulfur compounds reduced to H_2S which is recycled to Claus	200-500 ppmv H_2S	Feed to Claus	75-100%
Wellman-Lord	Wellman Power Gas	SO_2 in incinerator gas contacted with Na_2SO_3 to form $NaHSO_3$. Na_2SO_3 regenerated in evaporator/crystallizer.	<200 ppmv SO_2	Na_2SO_4/Na_2SO_3 crystals	130-150%

more favorable conditions, while the Beavon Process, the SCOT Process, and the Wellman-Lord Process are add-on units with higher efficiencies than the first three.

Additional tail gas treatment methods are described in detail in Appendix E (Volume 4).

Alternate Tail-Gas Treatment Methods--An alternate to the Claus unit and a modification of the unit are also being tested. The alternate, the UOP Sulfox Process, would produce no objectionable tail gas stream. The Mineral and Chemical Resource Company (MCRC)[115] is a modified improvement of the Claus process.

The UOP Sulfox Process[116]--The UOP Sulfox process is an alternative to the Claus process. In this process, aqueous ammonia, instead of an amine solution, is used to scrub H_2S from refinery streams. Ammonia is then scrubbed from the gas with purified water.

Hydrogen sulfide content in the treated gas is 10 to 100 ppm. It is possible, at increased cost, to design a Sulfox unit which can achieve 1 ppm H_2S in the tail gas. However, NSPS requires less than 250 ppmv SO_2 from a final oxidizing step, which in this case would probably be interpreted as "SO_2 or its equivalent as reduced sulfur compounds."

It may be possible to convert an existing Claus system to a Sulfox System with a minimum of expense. It is probable that the existing amine absorber could be used as the ammonia absorber and that the existing amine stripper could be used in the Sulfox unit proper.

Cost of a Sulfox system is considered about equal to that of a Claus unit, not including the cost of tail-gas cleaning. Utility costs are estimated to be about 60 percent of those of a Claus unit.

The Mineral and Chemical Resource Company (MCRC)[115]--The MCRC Sulfur Recovery process is actually a modified improvement of the Claus process. A proprietary scrubber is used to improve sulfur recovery and also to remove any ammonium sulfate which forms in a Claus unit if the feed contains ammonia. A 98 percent sulfur recovery efficiency can be obtained with a three converter design; greater than 99 percent efficiency can be obtained with four converters. Two MCRC sulfur recovery plants have been operating since 1976.

Control Technology for Sulfur Recovery in Other Industries--Some FGD processes developed by the electric utility industry may be applicable to the flue gas from a Claus incinerator. These processes are summarized in Table 7-59.

7.2.2.2 Catalyst Regeneration

Catalysts are used in several petroleum refining operations, namely, fluid catalytic cracking (FCC), moving bed catalytic cracking (TCC), catalytic hydrocracking, reforming, and various oil desulfurizations. These catalysts become coated with carbon and metals and must be regenerated to restore their activity. During regeneration, the carbon is oxidized to CO and CO_2. Hydrocarbons may be incompletely burned.

In most applications, a catalyst must be regenerated only a few times a year. Emissions during these episodes may include catalyst fumes, oil mist, hydrocarbons, ammonia, SO_x, chlorides, cyanides, NO_x, CO, and aerosols. Though there may be significant emissions during the regeneration of some of these catalysts, the total emissions over the course of a year are probably not significant.

Catalytic cracking catalyst regeneration is a continuous process. Uncontrolled cracking catalyst regeneration can be a major source of air

TABLE 7-59. FLUE GAS DESULFURIZATION PROCESS

Name	Developer	Description	Number of Commercial Units	Efficiency of SO_2 Removal or SO_2 Concentration in flue gas	Product	Approximate Cost, % Cost of Claus Unit
Thoroughbred 101 Process	Chiyoda Chem. Eng. and Construction Company, Ltd.	Tail gas incineration followed by Absorption of SO_2 in dilute sulfuric acid.	9	<500ppmv SO_2	Gypsum	--
Citrate Process	U.S. Bureau of Mines	Absorption of SO_2 in aqueous sodium citrate solution. Absorber liquor is regenerated with H_2S	None	95-99%	S_o	250
Townsend Process	F.M. Townsend	Claus reaction takes place in an organic solvent, such as methylene gylcol, at an elevated temperature.	None	--	S_o	--
Lurgi-Claus-Abgas-Schwefelgewinnung (LUCAS)	Lurgi	Incineration + hot coke to convert sulfur compounds to SO_2. SO_2 removed with aqueous alkali phosphate solution which is regenerable.	One	99% (<200ppm SO_2, <150ppm COS/CS_2)	S_o (from Claus)	75-80
Takahak Process		Tail gas contacted with sodium carbonate and redox catalyst.		99.9%	S_o	

pollution in a petroleum refinery. Flue gases from catalytic cracker regenerators contain particulates, SO_x, carbon monoxide, hydrocarbons, NO_x, aldehydes and ammonia.

Existing Control Technology for Catalyst Regeneration--The existing method for controlling CO emissions from catalyst regeneration in catalytic cracking units is combustion in CO boilers. The CO in the regenerator flue gas is burned to CO_2, and the heat is recovered as steam in a waste heat boiler. Particulate emissions can be controlled by cyclones followed by either electrostatic precipitators or scrubbers.

The effectiveness of combined CO combustion and particulate removal in controlling emissions from catalyst regeneration are presented in Section 7.1. The amount of CO is reduced, of course. However, another noticeable result is the substantial reduction in emissions of hydrocarbons, ammonia, and aldehydes. The exiting flue gas temperature is much lower after passing through the CO boiler.

Control Technology in Other Industries for Catalyst Regeneration--Several FGD methods used by the utility industry have been proposed for use on FCC regenerators.[117] They are discussed below. In addition, some of the regenerable processes discussed in this section for treatment of the Claus unit tail gas may also be applicable. One of the processes described below simultaneously removes SO_x and particulates from the flue gas.

The Lime/Limestone FGD Process[118]--Lime or limestone FGD processes are the most widely used FGD systems. The systems are very similar; they consume large quantities of feed material and produce large quantities of waste sludge, but have relatively low operating costs and are highly reliable. An SO_2 removal efficiency of greater than 90 percent has been demonstrated.

A major design option is the choice of lime or limestone. Limestone is less expensive than lime, but it is not used as efficiently by the process; therefore, there is more feed material consumption and more waste sludge production. Procedures which improve limestone utilization also increase capital and operating costs.

Lime systems are usually more expensive to operate, however, because of the high cost of lime. Lime systems may be preferred where space is limited for feed material processing and/or waste sludge disposal. Capital and utility costs are also lower for a lime system. The choice between lime and limestone is also influenced by the availability of raw materials.

Costs of raw materials and utilities for lime/limestone systems are generally lower than for regenerable processes, although more raw materials are required. Annual operating costs of a lime system are about seven percent higher than those of a limestone system.

The Dual Alkali FGD Process[119]--The dual alkali (or double alkali) FGD process can be used to overcome the scaling problem inherent in lime/limestone FGD systems, while retaining the convenience of solid waste disposal. There are 53 operating dual alkali systems in the United States and Japan; several more are under construction.

These systems can achieve SO_2 removal efficiencies of greater than 90 percent. The capability for more than 99 percent removal of SO_2 has been demonstrated. The dual alkali process itself is capable of greater than 98 percent particle removal.

Absorption of SO_2 from the flue gas takes place in a tray tower, or a venturi scrubber if simultaneous particle removal is desired. The SO_2 in the flue gas reacts primarily with sodium sulfite (Na_2SO_3) to form sodium bisulfite ($NaHSO_3$). Some sulfite and bisulfite oxidize to sulfate.

The desulfurized flue gas is reheated if necessary and released to a stack. A bleed stream of the scrubbing liquor is withdrawn continuously from the absorber and regenerated.

Loss of soluble sodium and nonsulfur calcium salts can create water pollution problems and also a loss of raw materials. Therefore, water can be added to the system only to replace that lost through evaporation or in the solid waste product. Also, retention of soluble salts by the solid waste must be minimized.

Sludge from the dual alkali process must be fixed chemically to decrease its permeability and leachability, or it must be disposed of in well-designed lined ponds. The thixotropic nature of the calcium sulfite may make land reclamation difficult. A larger disposal area will be required then for a lime/limestone system.

Dual alkali systems are economically competitive with lime/limestone systems.

7.2.2.3 Boilers and Process Heaters[120]

Most refineries use steam boilers to provide steam for direct use in various processes, for heating and for driving steam turbines. Process heaters are used extensively in refining operations. They are the largest combustion source of hydrocarbons in a refinery. Refinery boilers and heaters are fired with most available fuel.

Existing Control Technology for Heaters and Boilers--Emissions from boilers and process heaters depend on the operating parameters of the unit and the fuel burned. Emission factors for burning natural gas and residual fuel oil are given in Section 7.1.

In addition to the combustion emissions, there are also emissions associated with the decoking of the heaters. At intervals of about six months to three years, each heater must be flushed with a steam-air mixture to remove interior coke deposits. Emissions are similar to those from decoking the delayed coking unit, but they are smaller and more infrequent.

Control Technologies Available in Refineries for Heaters and Boilers--Emissions of SO_x from boilers and process heaters can be minimized by routing the flue gas to an integrated sulfur removal facility such as the IFP-150 and the Aquaclaus. However, there are substantial problems to this approach. This is discussed further in Appendix E (Volume 4).

NO_x Removal--NO_x emissions can be reduced by several tail-gas cleaning methods, but this is inherently more difficult than controlling NO_x by combustion modification techniques. The principal difficulties are the large amount of hot gas to be handled, the dilute concentration of NO_x, interferences by other pollutants and the high power consumption. Three methods for removal of NO_x from stack gases are gas scrubbing, catalytic reduction and thermal reduction with added ammonia. Because of economic considerations, only thermal reduction with added ammonia appears promising. This process is more expensive than combustion modifications but can supplement these modifications when stricter control of NO_x is required.

As with SO_x controls, substantial problems associated with flue gas collection exist in refineries.

Control Technology Available in Other Industries for Heaters and Boilers--Processes described previously in Section 7.2.2.2 for control of SO_2 emissions from FCCU regenerators may also be applicable to the flue gases from boilers and process heaters. Another process, the Shell Flue Gas Desulfurization process (SFGD) can be used to simultaneously remove SO_x and NO_x from process heater flue gas, fluid catalytic cracking regeneration, and Claus units. However, these flue gases would have to be collected and sent to one or two SFGD units. There are serious safety and economic obstacles to such a collection system.

The SFGD process has demonstrated SO_2 and NO_x removal efficiencies of greater than 90 percent. The efficiency of the system is not affected by variations in the SO_2 or NO_x concentration. The primary product of the process is SO_2, which may be sold, processed into elemental sulfur or sulfuric acid, or routed to the front of the Claus unit. The primary waste from the process is water generated during the recycle step. It generally contains 30 to 50 ppm dissolved SO_2. The SFGD process requires approximately two moles of hydrogen per mole of SO_2 removed and one mole of ammonia per mole of NO_x removed. A heat credit may be realized by the process. Actual costs for an integrated SFGD system are not available because such a system has not yet been built at a U.S. installation. Due to the complexity of the process, space requirements are expected to be high. Retrofit application of the SFGD process might be difficult because of the duct work required.

7.2.2.4 Vacuum Distillation

Certain control methods can virtually eliminate the process emissions from vacuum distillation. Emissions of noncondensable vapors are controlled by venting into a blowdown system or by incineration. The vapors may be used as supplemental fuel in process heaters and boilers. Oily condensate emissions can be eliminated by the use of mechanical vacuum pumps or surface condensers which discharge to a closed drainage system. Both noncondensable and condensable emissions can be minimized by the installation of a lean-oil absorption unit between the vacuum tower and the first stage vacuum jet.

7.2.2.5 Coking

There are two accepted methods for coking: fluid coking and delayed coking. Delayed coking is the more widely used method.

In the delayed coking process, the feed stream is heated and transferred to a coke drum which provides the proper residence time, pressure, and temperature for coking. When the coke drum has been filled to capacity, the coke is cut from the walls with high-pressure water; hydrocarbons and particulates are emitted when coke is removed.

Particulate emissions from the delayed coking process can be minimized by wetting down the coke during the removal procedure. Hydrocarbon emissions can be minimized by venting the quenching steam to a vapor recovery or blowdown system. Once the drum has cooled to 212°F, the steam purge can be replaced by a water flood. Further cooling will minimize steam and hydrocarbon vaporization when the drum is opened.

Fluid coking is a continuous process in which the feed is injected into a fluidized bed of hot coke particles. Approximately 30 pounds of carbon monoxide and about 520 pounds of particulates per 1,000 barrels of feed are emitted from an uncontrolled fluid coking unit.[7,121] There are often additional pollutants from coke combustion. Emissions can be controlled by the use of a scrubber or electrostatic precipitator and a CO boiler (either a separate one or the boiler which serves the catalytic cracking unit).

Significant particulate emissions often occur during the loading of coke into rail cars or trucks. An induced draft particulate control system using bag filters could reduce these emissions, but would be expensive to design, install, and maintain. A more reasonable approach is to spray the coke with a small amount of heavy crude oil or coker gas oil as it leaves the coker.

7.2.2.6 Air Blowing

Blowing air through a material may serve to oxidize, remove moisture, strip spent chemicals or mix the material. The amount of emissions produced by air blowing depends on the amount of air used per ton of charge, the volatility of the charge, and the temperature of the operation. In all of its uses, uncontrolled air blowing produces noxious odors.

Air is sometimes blown through asphalt to oxidize it and therefore increase its melting temperature and its hardness. Emissions from asphalt blowing are lessened by the fact that asphalt material is distilled at high temperatures before it is subjected to asphalt blowing. Available data indicate uncontrolled emissions from asphalt blowing to be 40 to 80 pounds of hydrocarbons per ton of asphalt treated.[70]

Emissions from asphalt blowing can be reduced by vapor scrubbing, incineration, or a combination of both. Vapor scrubbers condense steam, aerosols, and essentially all of the hydrocarbon vapors. Incineration may be accomplished in process heaters, boilers, or flares. Hydrocarbon emissions from a controlled asphalt-blowing unit are negligible.[122]

Air blowing of gas oil products to remove moisture takes place in a packed tower or vessel. The exhausted air does contain some lighter hydrocarbon components of the gas oil.

In many refineries, air-blown brightening units have been replaced with packed vessels containing solid adsorbents.[120] These units have slight potential for process hydrocarbon emissions.

7.2.2.7 Chemical Sweetening

Chemical sweetening rids hydrocarbons of odorous mercaptans. Only low-sulfur (sweet) materials are subjected to this treatment; more drastic sulfur removal methods such as hydrodesulfurization are used for high sulfur (sour) materials.

In extractive sweetening, an aqueous NaOH or KOH solution extracts the sulfur. Before disposal, hydrocarbons are removed from the aqueous solution by inert-gas stripping, which may be a source of hydrocarbon emissions.

Catalysts are used to promote oxidative sweetening. Air is the oxidizing agent and is also used to regenerate the catalyst. Hydrocarbon emissions may result from both the oxidation and the regeneration steps.

Emissions from the inert gas stripping of spent caustic can be prevented by venting the gases to a flare or a furnace firebox.

Emissions from air blowing regeneration of spent oxidative sweetening solutions can be reduced by steam-stripping the spent solutions to recover hydrocarbons before air-blowing. The gaseous effluent from air blowing can then be incinerated to dispose of residual hydrocarbons.

7.2.2.8 Acid Treating

Hydrocarbon streams may be treated with acid to remove or dissolve undesirable materials. The use of sulfuric acid results in a hydrocarbon/acid sludge which is removed by clay filtration. To recover the acid, the sludge may be incinerated and the resultant SO_2 used to produce more sulfuric acid. Alternatively the hydrolysis-concentration process may be used; hot gases from the combustion of oil or gas are bubbled through the sludge to volatilize the hydrocarbon diluent and to concentrate the acid. Off-gases pass through a mist eliminator to the atmosphere. These gases may contain hydrocarbons and SO_2.

If the acid concentration process is used, the off-gases from the mist eliminator can be vented to caustic scrubbers for SO_2 and odorant removal, and then to an incinerator or a flare.

Hydrocarbons escaping from acid recovery operations can be eliminated by using acid regeneration. Regeneration involves sludge incineration to produce SO_2, which can be converted to H_2SO_4. Control methods are available for control of SO_2 emissions from acid sludge incineration.

7.2.2.9 Blowdown Systems

All units and equipment subject to shutdowns, upsets, emergency venting, or purging are manifolded into a multi-pressure collection system. Because the blowdown system receives materials from all processing units within the plant, any volatile material found in any process stream may be emitted from an uncontrolled blowdown system. It is estimated that 580 pounds of hydrocarbons per 1,000 barrels of refinery feed are emitted from an uncontrolled blowdown system.[7]

Blowdown emissions can be effectively controlled by venting into an integrated vapor-liquid recovery system. A series of flash drums and condensers arranged in descending operating pressures separate the blowdown into vapor pressure cuts. The liquid cuts are recycled to the refinery; the gaseous cuts are recycled or flared.

Emissions from a controlled blowdown system have been estimated to be 0.8 lb per 1,000 barrels of refinery feed, compared to 580 lb per

1,000 barrels for uncontrolled. The control is estimated to be 99.9 percent effective.[7]

7.2.2.10 Compressor Engines

Reciprocating and gas turbine engines fired with natural gas or refinery fuel gas are often used in older refineries to run high-pressure compressors. Their use is expected to decline.[120]

The exhaust emissions from these engines include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes, and depending on the sulfur content of the fuel, sulfur compounds. Emission factors for reciprocating and gas turbine compressor engines fired with natural gas are given in Table 7-60. Particulate values were not available.

No pollution control devices for refinery compressor engines are in current use.[7] Combustion modification is discussed in the following section.

7.2.3 Emission Reduction Through Process Modification

A reduction in emissions can sometimes be achieved as a result of process modifications made in the refinery. Changes in operating practices, the use of alternate fuels, and the hydroprocessing of refinery feedstocks can result in net reductions in emissions.

7.2.3.1 Alternative Operating Practices and Conditions

Regeneration of Catalytic Cracking Catalysts[123,124,125,126,127] Older FCC regenerators were designed for operation at temperatures up to 1150°F; the introduction of newer, more coke-sensitive catalysts necessitated higher temperatures. By 1976, 30 percent of all FCC regenerators were operating at 1300°F. High-temperature conversion of CO to CO_2

TABLE 7-60. EMISSION FACTORS FOR RECIPROCATING AND GAS TURBINE COMPRESSOR FUELED WITH NATURAL GAS

	Pollutant, lb/10^3 ft^3 gas burned			
Engine Type	NO_x as NO_2[a]	CO	HC as C[b]	SO_x as SO_2[c]
Reciprocating	3.4	0.43	1.4	2S
Gas Turbine	0.3	0.12	0.02	2S

[a] At rated load. In general, NO_x emissions increase with increasing load and intake air temperature. They generally decrease with increasing air-fuel ratios and absolute humidity.

[b] Overall less than one percent by weight is methane.

[c] S=Refinery gas sulfur content (lb/1000 SCF): factors based on 100% combustion of $S \rightarrow SO_2$.

Source: Reference 127.

generally occurs at 1,400 to 1,500°F. With high-temperature regeneration, the CO level in the exit gas from the regenerator can be reduced to well below 500 ppm. Thus, a CO boiler is no longer necessary for CO emission control.

Complete combustion of CO within the regenerator offers other emissions benefits in addition to reducing CO to less than 500 ppm: for example, elimination of the need for CO boiler reduces other emissions since auxiliary fuel burning is not required and NO_x-producing CO boiler temperatures are avoided. Recovery of additional heat in the regenerator reduces (and in some cases eliminates) the need for a FCC preheater and its associated emissions.

Several new catalysts, or promoters, have been introduced in the last several years to promote the combustion of CO to CO_2. A promoter may be chosen to promote complete combustion or partial combustion where metallurgy cannot withstand the higher temperatures.

In 1975, the cost of converting a relatively modern FCCU with stainless steel cyclones to high-temperature regeneration was $50,000 to $300,000. Cost of a CO boiler for the unit was perhaps $2 million to $3 million.

Other FCC operations which affect regenerator emissions are the amount of recycle and the stripping steam rate. Higher recycle rates produce more flue gas, but the net effect is negligible when compared to the impact of recycle on yields and operating costs. Similarly, insufficient stripping steam allows hydrocarbons to enter the regenerator to produce more flue gas and possible unstable operation. In this case, the impact of stripping steam rate on the entire unit's performance provides incentives for the reduction of emissions.

SO_x Removal in the FCC Regenerators[18,117]--Amoco has developed a catalyst which reduces the amount of sulfur leaving the regenerator as SO_2. The catalyst holds the sulfur until it is returned to the reactor, where it is released and converted to H_2S. The H_2S leaves the reactor with the cracked product and is later converted to sulfur in the Claus plant; the regenerated catalyst returns to the regenerator.

Cost for the 60 to 75 percent reduction in SO_x emissions with this method in a new facility is estimated at 3¢/bbl, compared to 22¢ to 24¢/bbl for stack-gas scrubbing and up to 27¢/bbl for feed hydrosulfurization. The use of the catalyst for SO_x control is also less expensive than other methods of retrofit applications.

Combustion Modification for Control of NO_x[46,128,129]--In combustion sources, NO may be produced either by the fixation of atmospheric nitrogen in the flame (thermal NO_x) or by the oxidation of a portion of the nitrogen in the fuel (fuel NO_x). NO_2 from combustion sources is produced as the NO combines with oxygen in the atmosphere.

Boilers, Furnaces, and Process Heaters--Combustion modifications for NO_x control on boilers, furnaces, and process heaters are of three general types: lowering the flame temperature, limiting the amount of excess air, and limiting the residence time within the flame. Control of NO_x is often counter to a high thermal efficiency and contributes to the emission of other undesirable substances. As a result, compromises must often be made.

A number of specific combustion modifications for NO_x control have been devised. The effectiveness of some of the individual methods and some combinations at different boiler loads are shown in Table 7-61.

Internal Combustion Engines--There are several modifications for controlling NO_x emissions from internal combustion engines. The percent

TABLE 7-61. REDUCTIONS OF NO_x EMISSIONS WITH COMBUSTION MODIFICATIONS AT VARIOUS BOILER LOADS

Combustion Modification		PERCENT REDUCTION IN NO_x EMISSIONS WITH														
		Low Excess Air			Staging			Low Excess Air and Staging			Flue Gas Recirculation			Possible* Combined Modifications		
(Percent Full Load)		85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60
Fuel Fired	Burner Arrangement															
Gas	Front Wall	13	24	7	37	30	30	48	42	36	-	-	-	43	42	36
	Horizontally Opposed	17	15	32	54	35	59	61	48	68	-	-	20	73	52	72
	Tangential	-	-	-	-	-	-	-	-	-	-	60	-	66	65	-
	Average	16	19	26	45	31	52	54	44	52	-	60	20	64	51	60
Oil	Front wall	27	20	28	29	20	20	39	32	21	46	31	-	50	41	21
	Horizontally Opposed	10	16	12	34	34	47	35	44	42	-	-	-	38	35	55
	Tangential	28	22	-	-	17	-	-	45	-	10	13	-	-	59	-
	Average	19	19	18	30	22	34	38	37	37	28	23	-	47	42	38

*Possible combination of modifications on the boilers tested.

Source: Reference 46.

NO_x reduction and the limitations for each of these modifications are given in Table 7-62. These methods are described in more detail in Appendix E (Volume 4).

7.2.3.2 Alternative Fuels [7]

Refiners traditionally have had a choice of natural gas, refinery gas, or distillate or residual fuel oils as fuel for refinery boilers and process heaters. The present trend is toward the heavier oils, both for economic reasons and because lighter oils are being reserved for smaller consumers with fewer emissions controls. This trend, however, results in higher emissions from refinery boilers and heaters.

Emissions factors for the use of natural gas and fuel oils in industrial boilers have been presented previously in Section 7.1. According to these factors, particulate emissions from natural gas and No. 2 oil are independent of sulfur content, but increased with sulfur content for No. 4 oil and heavier oil. Sulfur dioxide emissions are, of course, directly related to sulfur content of the fuel gas or oil.

Table 7-63 presents comparative emissions for natural gas and fuel oils for 10^6 Btu heat release. The AP-42-based "average" natural gas contains only about 22 percent of the sulfur equivalent allowed by NSPS (0.10 grain/10 ft^3 gas) (Column 1). Fuel oils containing 0.3 to 2.0 weight percent sulfur, which represent the broad range of sulfur levels in fuels, emit from 500 to 3,600 times as much SO_x as the "average" natural gas.

Overall, the substitution of fuel oils for natural gas without instituting additional controls will have a detrimental impact on the environment.

TABLE 7-62. ENGINE MODIFICATIONS WHICH REDUCE NO_x EMISSIONS FROM INTERNAL COMBUSTION ENGINES

	DIESELS		SPARK IGNITION		GAS TURBINES	
ENGINE MODIFICATION	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS
Combustion chamber design	40	Increased first cost	-	Not applicable	Under development	
Fuel properties	Variable	Availability of low nitrogen fuels; higher operating cost	Variable	Availability of low nitrogen fuels; higher operating costs	Variable	Availability of low nitrogen fuels; higher operating costs
Air/fuel ratio	-	Not applicable	30	Backfiring; reduced power	50	Increased fuel; decreased power
Exhaust recycle	50	Increased fuel; decreased power	50	Increased fuel; decreased power	Under development	
Fuel injection timing	40	Increased fuel; decreased power	-	Not applicable	-	Not applicable
Steam or water injection	50	Corrosion problems	50	Corrosion problems	75	Need deiorized water; costly
Variable compression ratio	Under development		-	Not applicable	-	Not applicable

Source: Reference 46.

TABLE 7-63. REFINERY FUEL EMISSIONS AT EQUIVALENT HEAT RELEASE

Fuel Type	Natural Gas[a]	#2 F.O.[a]	#6 F.O.[a]
Gross Heating Value	1012 Btu/ft^3[b]	19,460 Btu/lb[a]	18,200 Btu/lb[a]
Specific Gravity	0.55/Air	0.856/water	0.972/water[a]
Amount Equivalent to 10^6 Btu heat release	988 ft^3	7.20 gal	6.78 gal
Emissions lb per 10^6 Btu:			
SO_2: NSPS	2.66×10^{-3}[c]		
SO_2: (av)	5.9×10^{-4}	0.306	2.13
Particulates (av)	9.9×10^{-3}	0.014	0.16
CO	1.68×10^{-3}	0.036	0.034
HC	3.0×10^{-3}	7.2×10^{-3}	6.8×10^{-3}
NO_x (av)	0.17	0.16	0.41
Sulfur Wt% (oils only)		0.3 (typical)	2.0 (high)[d]

[a] Reference 7.

[b] Accepted value for pure methane.

[c] NSPS emission limit of SO_2 $= \frac{0.1 \text{ gr } H_2S}{10 \text{ ft}^3 \text{ nat. gas}} \times \frac{64 \text{ lb } SO_2}{34 \text{ lb } H_2S} \times \frac{1 \text{ lb}}{7000 \text{ gr}}$

$$= 2.69 \times 10^{-6} \frac{\text{lb } SO_2}{\text{ft}^3 \text{ nat. gas}}$$

[d] Residual fuel oil sulfur levels range from 0.3 Wt. percent (N.Y. City) to 2.0 percent (Midwest) according to sales data as regularly published in Oil and Gas Journal

7.2.3.3 Hydroprocessing as Feedstock Pretreatment

Hydroprocessing includes those processes in which hydrogen is combined with a feedstock and passed over a catalyst at elevated temperature and pressure. Some examples are:

- Hydrodesulfurization of residual feedstock to be used in fuel oil production or catalytic cracking.
- Hydrodesulfurization of heavy gas oils and middle distillates to be used in the production of jet fuels, diesel fuels, and heating oils.
- Hydrodesulfurization of heavy gas oils to be used as high-quality catalytic cracking feed.
- Hydrodesulfurization and hydrodenitrogenation of naphtha and straight-run crude distillate streams to be used as primary feeds for the isomerization and catalytic reforming units.

These and other uses of hydroprocessing are discussed more thoroughly in Section 4.4 of Appendix F (volume 5).

Hydroprocessing removes sulfur and nitrogen-containing compounds, the heavy metals, oxygen, and halides. Hydrotreating also stabilizes unsaturated hydrocarbons by saturating the double bonds.

The overall impact of hydroprocessing is generally beneficial for reducing emissions. Removal of objectionable materials, besides reducing emissions from subsequent processes, can significantly reduce catalyst poisoning and equipment corrosion and can also increase yields. Hydrodesulfurization of catalytic cracking unit feeds is a very effective method for reducing sulfur emissions from catalytic cracking catalyst regeneration.

8.0 ENVIRONMENTAL ASSESSMENT

An environmental assessment was performed to examine the effects of refinery emissions on the surrounding atmosphere. The large volumes of emission rate data generated in this program were used to predict ambient pollutant levels. Environmental and public health effects of the predicted pollutant concentrations were also examined. Finally, a brief survey of the effects of existing and potential regulatory policies and developing technology was made.

The primary objective of the environmental assessment is to provide guidance in identifying potential problem areas. For instance, it can provide insight into which sources and which pollutants appear to pose potential hazards. The results are semi-quantitative in nature, which allows a relative ranking of such problem areas. This can help to focus attention on those areas needing further research. The environmental assessment is only a tool to aid in the relative evaluation of potential environmental impacts, not a method for making precise and accurate predictions of such impacts. The results should not be regarded as an absolute value which can be used to predict violations of standards, public health hazards, requirements for additional pollution control technology, or regulatory requirements.

The complete environmental assessment of petroleum refineries is presented in Appendix D (Volume 4) of this report. The methodology used in performing the environmental assessment is described in Sections 8.1 through 8.3. Section 8.1 describes the hypothetical refinery model used in the assessment. The calculations used are shown in Section 8.2. The workings of the atmospheric dispersion model are described in Section 8.3. Section 8.4 conveys the predictive results of the model applied to the air quality surrounding the hypothetical refinery. Effects of existing and potential environmental regulations and policies on refineries and their surrounding environments are discussed in Section 8.5.

The environmental assessment performed in this study included the following steps:

- Definition of a model refinery.
- Calculation of emissions from the model refinery.
- Calculation of ground level concentrations outside the boundaries of the refinery using atmospheric dispersion modeling.
- Comparison of those ground level concentrations to some acceptable concentration.

The parameter which is used to quantify environmental impacts is called source severity. This concept was developed by Monsanto Research Corporation under contract to the EPA.[130]

A source severity factor is defined as the ratio of the maximum ground level concentration of a pollutant in a "standard receiving atmosphere" to the "acceptable pollutant concentration," as shown below:

$$S = \frac{\bar{\chi}_{max}}{F}$$

where

S = the source severity factor,

$\bar{\chi}_{max}$ = the maximum ground level concentration of the pollutant, and

F = the acceptable pollutant concentration.

This acceptable concentration is derived from either National Ambient Air Quality Standards (NAAQS) or from Threshold Limit Values (TLV's). If the resulting ratio is greater than 1.0, then emission reduction is probably needed. If the ratio is below about 0.01, then further reduction is probably not needed. Emission reduction requirements for pollutants with source severity factors between 0.01 and 1.0 are uncertain.

8.1 Definition of the Refinery Model

The first element to be examined is the development of the model refinery. Both the refinery processing arrangement and its physical configuration must be characterized. There is ample documentation of the difficulties involved in trying to synthesize a "typical representative refinery." Refineries are very diverse, and only a very rough approximation can be achieved with a single model. Therefore, it should be noted throughout this discussion that this is not a model that attempts to represent the total industry, but rather a model of one hypothetical refinery that reflects the "real world" as much as possible.

The source for the model refinery is an EPA report prepared by Pacific Environmental Services.[49] The "Large Existing Refinery" case was chosen as the model for this study because it is essentially a worst case. If the results show minimal environmental impact for this type of refinery, then smaller, less complex, or more efficient grass roots refineries should create an even lesser impact.

8.1.1 Refinery Process Configuration

Figure 8-1 shows the basic processing configuration of the model refinery. All of the normal refinery unit operations are represented. Approximately 350,000 barrels per day of crude can be processed in the model refinery. It is a reasonable example of a modern fuels refinery supplying low sulfur products.

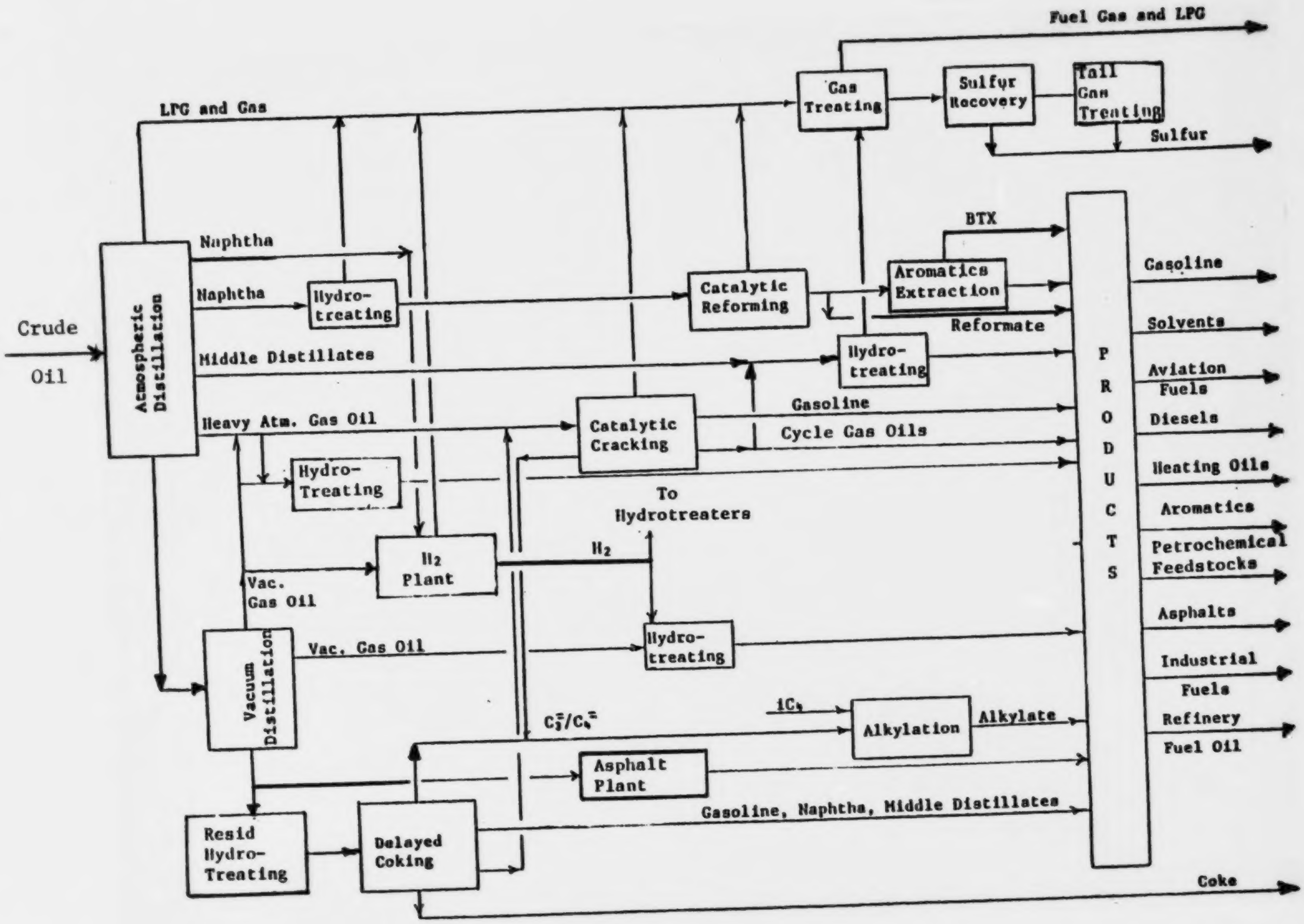

Fuel Gas and LPG
LPG and Gas
Gas Treating
Sulfur Recovery
Tail Gas Treating
Sulfur
Crude Oil
Atmospheric Distillation
Naphtha
Naphtha
Hydro-treating
Catalytic Reforming
BTX
Aromatics Extraction
Reformate
Middle Distillates
Hydro-treating
Heavy Atm. Gas Oil
Catalytic Cracking
Gasoline
Cycle Gas Oils
Hydro-Treating
To Hydrotreaters
H_2 Plant
H_2
Vac. Gas Oil
Vacuum Distillation
Vac. Gas Oil
Hydro-treating
iC_4
Alkylation
Alkylate
$C_3^=/C_4^=$
Asphalt Plant
Resid Hydro-Treating
Delayed Coking
Gasoline, Naphtha, Middle Distillates
P R O D U C T S
Gasoline
Solvents
Aviation Fuels
Diesels
Heating Oils
Aromatics
Petrochemical Feedstocks
Asphalts
Industrial Fuels
Refinery Fuel Oil
Coke

Figure 8-1. Block Flow Diagram of Model Refinery

8.1.2 Refinery Layout

The plot plan of the refinery is shown in Figure 8-2. The functions of the various refinery modules are detailed in Table 8-1. This environmental assessment does not include the effects of emissions from storage tanks (This is discussed further in Section 8.4.3). It includes only emissions from the refinery processes. The process areas tend to form two clusters, probably the result of a stage-wise expansion over a period of many years. Considerable detail has been included in the physical model. All of the appropriate vital functions have been accounted for and distributed in a realistic manner.

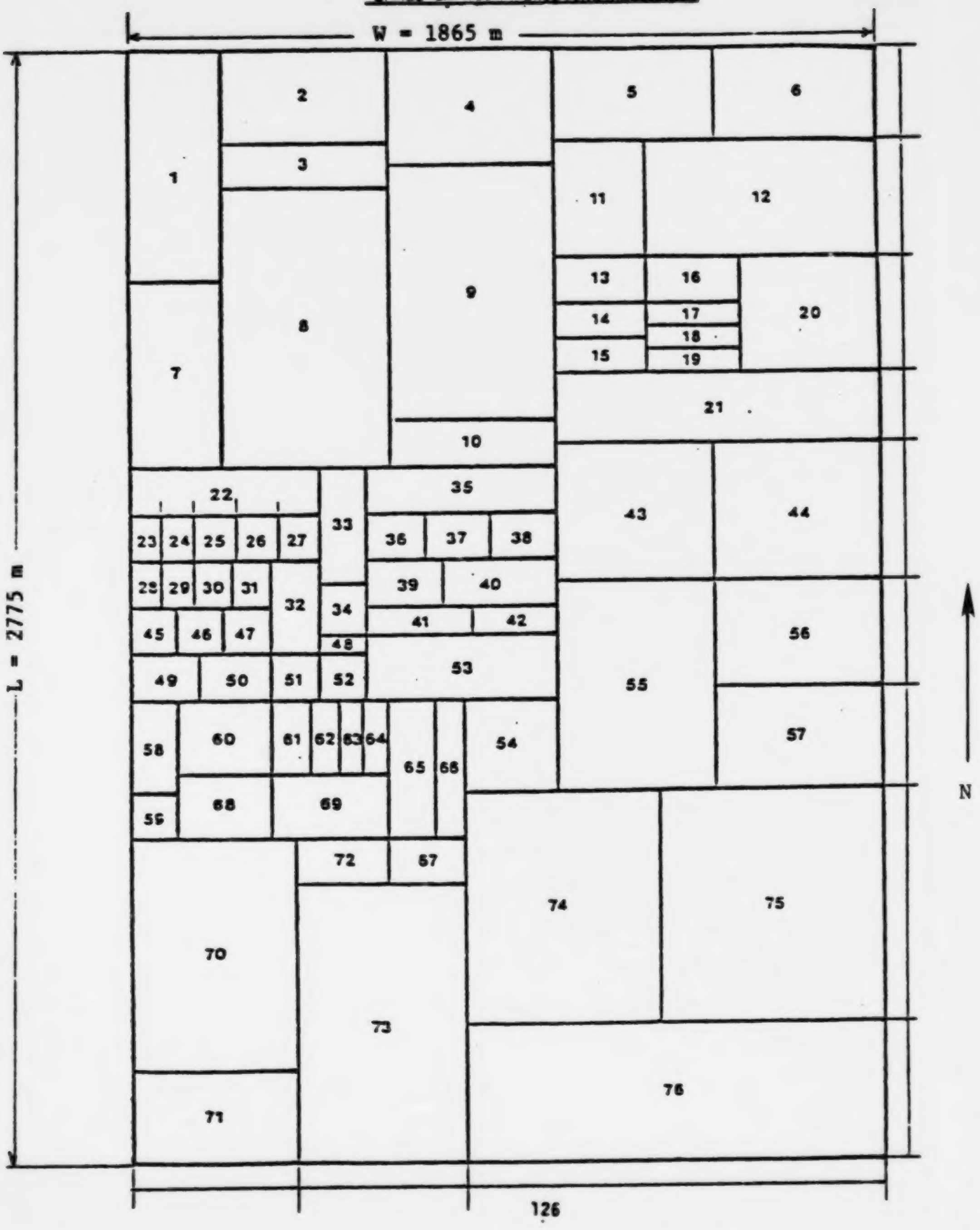
8.2 Emission Calculations

This section describes the estimation of losses using emission factors and fitting counts. Also included are the hydrocarbon emissions broken down into their component compounds.

8.2.1 Emission Factors and Fitting Counts

The emission factors required for the calculations were derived primarily from the results of testing on this program, but they were supplemented by emission factors from other sources (such as AP-42[7]) as needed. Fugitive emission factors for valves, pumps, compressors, flanges, relief valves, drains, and cooling towers were developed in this program. Estimated fitting counts and emission factors for fugitive sources in the model refinery are presented in Table 8-2. Emission factors for process sources and the corresponding source capacities are given in Table 8-3.

The estimate of the population of each type of fitting is as important as the emission factor in determining total emissions. The PES model contained estimates of fitting populations, but they were not


LARGE CAPACITY EXISTING REFINERY

W = 1865 m
L = 2775 m
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
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Figure 8-2. Model Refinery Layout[49]

TABLE 8-1. LARGE CAPACITY EXISTING REFINERY MODULE KEY[49]

Module No.	Description	Module No.	Description
L1	Buffer Zone	L36	Catalytic Reformer
L2	Feedstock Storage	L37	Aromatics Extraction
L3	Crude Oil Storage	L38	Catalytic Cracking
L4	Feedstock Storage	L39	Para-Xylene Plant
L5	Feedstock Storage	L40	Delayed Coker
L6	Crude Oil Storage	L41	Barrel Storage
L7	Feedstock and Product Storage	L42	Barrel Reconditioning
		L43	Feedstock Storage
L8	Crude, Feedstock, and Product Storage	L44	Storm Water Impound Basin
L9	Crude, Feedstock, and Product Storage	L45	Warehouse
		L46	Gas Holder/Blowdown Stack
L10	Oil-Water Separator		
L11	Product Storage	L47	Gas Holder/Blowdown Stack
L12	Product Storage		
L13	Distillation and Gas Recovery Unit	L48	Fire Prevention Training Facility
L14	Jet Hydrofiner/Catalytic Reformer	L49	Oil-Water Separator
		L50	Asphalt Plant
		L51	Solvent Treating Plant/Boiler House
L15	Naphtha Hydrotreater		
L16	Hydrotreater (Lt Cycle Oil)	L52	SO_2 Treating Plant/Tanks
L17	Hydrogen Manufacturing	L53	Lube Oil Packaging
L18	Partial Oxidation Unit	L54	Coke Storage
L19	Future Expansion	L55	Crude Oil Storage
L20	Cooling Tower	L56	Feedstock Storage
L21	Flares	L57	Tanks/Impound Basin
L22	Feedstock and Product Storage	L58	Administration
		L59	Oil-Water Separator
L23	Naphtha Hydrotreater	L60	Gasoline Sweetener/Crude Distillation
L24	Vacuum Gas Oil Unit		
L25	Benzene Fractionation	L61	Crude Distillation/Crude Desalter
L26	Steam Rerun Stills		
L27	Future Expansion	L62	Specialty Crude Distillation
L28	Crude Distillation		
L29	Catalytic Reformer	L63	Speciality Crude Distillation/Condenser Box
L30	Vacuum Residum Desulfurizer		
L31	Hydrogen Manufacturing	L64	Gasoline Fractionating Unit
L32	Alkylation		
L33	Distillate Hydrodesulfurization (Hvy Gas Oil)	L65	Tank Loading/Truck Loading/Vapor Recovery
L34	Sulfur Recovery	L66	Buildings
L35	Tanks/Cooling Towers	L67	LPG Storage and Blending
L68	Vapor Recovery/Gasoline Rectifier/Tanks		
L69	Main Pump House		
L70	Product Storage		
L71	Wastewater Treatment		
L72	Building		
L73	Product Storage		
L74	Shops and Warehouse		
L75	Crude Oil Storage		
L76	Crude, Feedstock, and Product Storage		

The oil/water separator in Module L10 treats aqueous discharge from Modules L1-L21.

The separator located in Module L59 treats aqueous streams from Modules L58-L60, L70, L71, and L73-L76.

The wastewater separator in Module L49 treats discharges from the remaining modules.

TABLE 8-2. FUGITIVE SOURCES AND EMISSION FACTORS

SOURCE	ESTIMATED POPULATION (OR CAPACITY)	SERVICE CATEGORY	NON-METHANE HYDROCARBON (NMHC) EMISSION FACTORS
Pump Seals[1]	313	Light Liquid	0.25 lb/hr./source
	340	Heavy Liquid	0.046
Valves[1]	1714	Hydrogen	0.018
	4198	HC Gas	0.059
	7422	Light Liquid	0.024
	8442	Heavy Liquid	0.0005
Compressor Seals[1]	82	Hydrogen	0.11
	48	HC Gas	1.40
Flanges[1]	84346	NA	0.00056
Relief Valves[1]	171	NA	0.19
Process Drains[1]	1105	NA	0.070
Cooling Towers[1]	(10,668 x 10^3 gal/hr)	NA	0.006 lb/10^3 gal.
Oil/Water Separators[2]	(160.3 x 10^3 gal/hr)	Uncontrolled	5.0 lb/10^3 gal.
	(1719 x 10^3 gal/hr)	Controlled	0.2 lb/10^3 gal.
Dissolved Air Flotation[1]	(220.5 x 10^3 gal/hr)	NA	(0.01 lb/10^3 gal.)[3]

[1] Emission factors based on Radian testing.

[2] Emission factors based on AP-42.[7]

[3] This value is a rough average of a very few test results. It should not be construed as an emission factor for broad application.

TABLE 8-3. PROCESS SOURCES AND EMISSION FACTORS

SOURCE	CAPACITY	EMISSION FACTORS				
		PARTICULATES	SO_x	NO_x	CO	NM HYDROCARBONS
Process Heaters/Boilers						
- oil fired[1]	36.7×10^3 gal/hr	6 lb/10^3 gal	47.7 lb/10^3 gal	60 lb/10^3 gal	5 lb/10^3 gal	1 lb/10^3 gal
- gas -fired[2]	2.27×10^6 ft^3/hr	5 lb/10^6 ft^3	0.6 lb/10^6 ft^3	120 lb/10^6 ft^3	17 lb/10^6 ft^3	3 lb/10^6 ft^3
Fluid Catalytic Cracker CO Boiler[3]	2.086×10^3Bbl/hr	45 lb/10^3Bbl	493 lb/10^3Bbl	71 lb/10^3Bbl	Negligible	13.3 lb/10^3Bbl
Sulfur Recovery Complex[4]						
- Claus plants plus Wellman-Lord Tail Gas Treating Unit	408 long tons/day (LTPD)	--	3.6 lb/LT	--	--	--
- Sulfuric Acid Plant	179 LTPD	--	14.6 lb/LT	--	--	--
Flares[5]	350×10^3Bbl/day	Negligible	26.9 lb/10^3Bbl	18.9 lb/10^3Bbl	4.3 lb/10^3Bbl	0.8 lb/10^3Bbl

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[1] Based on AP-42[7] factors for No. 6 Fuel Oil with 0.3 wt. % sulfur.

[2] Based on AP-42[7] factors for natural gas.

[3] Based on AP-42[7] factors for a Fluid Catalytic Cracker with an Electrostatic Precipitator and a CO Boiler, except the NMHC factor was taken from Radian testing.

[4] Based on sulfur recovery efficiencies taken from Hydrocarbon Processing;[4] 2-stage Claus = 92%, Wellman-Lord TGTU = 99%, Sulfuric Acid Plant = 99%

[5] Based on AP 42[7] factors for blowdown systems with vapor recovery and vents to flares.

broken down into the service categories corresponding to the emission factors. Radian data on fitting counts were generated during the field testing phase (see Tables 5-16 and 5-17 in Section 5). These unit configurations did not necessarily match those from the model refinery. The detailed procedure developed to generate fitting counts compatible with emission factor service classes and to represent the model refinery as closely as possible is described in Appendix D (Volume 4).

Although emissions from storage tanks were not within the scope of this study, they were estimated to provide a basis of comparison to other hydrocarbon emission sources. The PES report[49] contained a detailed breakdown of the storage facilities, their service, capacities, and annual turnover. Emission factors were taken from AP-42[7] and applied to these facilities to estimate total emissions. The PES data indicated the use of floating roofs to control emissions on all tanks containing liquids with Reid vapor pressures greater than 0.5 psia.

8.2.2 Emissions of Criteria Pollutants and Total Hydrocarbons

Applying all of these factors, a slate of refinery emissions was generated. Table 8-4 is a summary of those emissions by pollutant type.

8.2.3 Emissions of Selected Hydrocarbon Components

The emissions estimates given in Table 8-4 are sufficient to estimate the ambient concentrations of criteria pollutants, but a species breakdown is necessary to evaluate individual hydrocarbon concentrations. Analyses of the components in various process streams were made in this program and supplemented by literature sources. The application of these stream analyses is not straightforward, however, since the emissions were

TABLE 8-4. SUMMARY OF EMISSIONS FROM THE MODEL REFINERY

	Emissions in Tons/Year			
Pollutant	Point Sources[1]	Fugitives[2]	Storage	Total
Particulates	1,425	---	---	1,425
SO_x	14,650	---	---	14,650
CO	1,247	---	---	1,247
NO_x	12,693	---	---	12,693
Nonmethane Hydrocarbons	364	8,767	3,308	12,439

[1] Includes combustion sources, fluid catalytic cracker, CO boiler, sulfur recovery complex, and flares.

[2] Includes process fittings (pumps, valves, flanges, compressors, drains, and relief valves), cooling towers, oil/water separators, and other wastewater treating units.

calculated on a unit basis. The necessary approach involves three steps:

(1) Identification of the major product and intermediate streams in each unit. Total unit emissions were distributed among each stream.

(2) Application of stream analyses to estimate component emissions for each stream. Component analyses were obtained from samples taken during this program and were supplemented where necessary with data from a previous Radian literature survey,[131] an API medical research report,[132] and engineering estimates.

(3) Summation of the stream component emissions to get unit component emissions. In this assessment, some components were consolidated into groups if either discrete concentration data or quantifiable toxicity data were unavailable.

An example of the distribution of emissions between each process stream for valves in an FCC unit is given in Table 8-5. The estimated percentage of fittings on each stream is multiplied by the weighted average emission factor for fittings in that service. The result is the percentage of the total unit fugitive emissions attributed to each process stream. The weighted average emissions factor used in Table 8-5 may be a combination of the gas-light liquid, or the gas-heavy liquid emission factors if the particular process stream is present in the unit as both a gas and a liquid.

A summary of stream quality data is given in Table 8-6. This table shows the estimated component analysis for numerous refinery streams.

TABLE 8-5. DISTRIBUTION OF UNIT FUGITIVE EMISSIONS BY STREAM

	Example: Fluid Catalytic Cracking Unit			
Stream	Percent of Fittings in That Service Ⓐ	Mean Emission Factor in That Service Ⓑ lb/hr/source	Product Ⓐ x Ⓑ	Percent of Unit Fugitive Emissions in That Service
Atmospheric Gas Oil	15	0.0016	0.024	1
Fuel Gas	10	0.059	0.59	30
Olefinic LPG	15	0.030	0.45	23
Cracked Naphtha	30	0.030	0.9	45
Lt. Cycle Gas Oil	20	0.0016	0.032	1
Hvy. Cycle Gas Oil	10	0.0	0.0	0
Totals	100	N.A.	1.996	100

TABLE 8-6. SUMMARY OF STREAM QUALITY DATA (PPMW)[a]

Compound or Functional Family	Crude Oil	Straight Run Naphtha	Middle Distillate	Atmospheric Gas & Oil	Vacuum Gas & Oil	Reformate	H_2 Recycle Gas	Desulfurized Naphtha
Benzene	60	253	0	0	0	5,400	0	253
Toluene	680	2,621	5	8	5	77,700	0	2,621
Ethylbenzene	220	887	9	6	6	33,500	0	887
Xylenes	880	1,623	52	16	22	170,900	0	1,623
Other Alkylbenzenes	3,739	16,578	835	61	368	324,400	0	16,578
Naphthalene	260	1,463	100	4	28	7,400	0	1,463
Anthracene	140	5	56	3	12	0	0	5
Biphenyl	320	628	0	0	9	0	0	628
Other PNA's	7,880	14,983	5,507	220	663	700	0	14,983
n-Hexane	18,000	38,838	0	0	0	24,000	0	38,838
Other Alkanes	877,240	499,613	842,536	949,673	948,887	356,000	650,000	499,613
Olefins	0	0	0	0	0	0	0	0
Cycloalkanes	58,300	422,508	100,000	50,000	50,000	0	0	422,508
Other Compounds Indicated Present	Carbonyl $\simeq$ 500 ppm Thiols $\simeq$ 25,000 ppm Sulfides $\simeq$ 6,000 ppm Quinolines $\simeq$ 200 ppm Pyridines	Pyridines Thiols Sulfides	Pyridines Thiols Sulfides $\simeq$ 51,000 ppm Quinolines	Pyridines Thiols Sulfides Quinolines $\simeq$ 9 ppm	Pyridines Thiols Sulfides Quinolines		$H_2 \simeq$ 350,000	

Continued

TABLE 8-6. (Continued)

Compound or Functional Family	Hydrotreated Middle Distillate	Refinery Fuel Gas	Liquefied Petroleum Gas (LPG)	Raffinate	Aromatics Extract	Benzene	Toluene	Xylenes
Benzene	0	0	0	50	17,840	993,000	1,000	0
Toluene	5	0	0	750	256,700	2,000	992,800	1,000
Ethylbenzene	9	0	0	300	110,670	0	4,000	162,420
Xylenes	52	0	0	1,500	564,590	0	1,000	828,580
Other Alkylbenzenes	835	0	0	2,300	48,000	0	0	5,000
Naphthalene	100	0	0	50	100	0	0	100
Anthracene	56	0	0	0	0	0	0	0
Biphenyl	0	0	0	0	0	0	0	0
Other PNA's	5,507	0	0	50	100	0	0	100
n-Hexane	0	0	0	63,000	100	5,000	0	0
Other Alkanes	887,436	920,000	1,000,000	932,000	1,900	0	1,200	2,800
Olefins	0	60,000	0	0	0	0	0	0
Cycloalkanes	100,000	0	0	0	0	0	0	0
Other Compounds Indicated Present	Sulfides ≃ 6,000 ppm	$H_2 \simeq 20{,}000$ Thiols Sulfides	Thiols Sulfides					

(Continued)

TABLE 8-6. (Continued)

Compound or Functional Family	LPG Olefins	Alkylate	Cracked Naphtha	FCC Light Cycle Gas & Oil	FCC Heavy Cycle Gas & Oil	Heavy Aromatics Extract (SO_2 Plant)	Asphalt	API Separator Skim Oil	Vacuum Resid
Benzene	0	0.1	2,880	0	740	0	0	87	0
Toluene	0	0.3	89,780	40	10,000	0	0	1,713	0
Ethylbenzene	0	0.1	21,430	0	1,200	0	0	661	0
Xylenes	0	1.1	171,450	610	11,800	0	0	2,510	0
Other Alkylbenzenes	0	3.3	243,470	26,670	38,200	750,000	*i*[b]	12,751	*i*
Naphthalene	0	0.3	10,950	59,000	14,000	0	0	990	0
Anthracene	0	0	0	10,270	0	0	2	457	2
Biphenyl	0	0	0	10,180	0	0	0	2,351	0
Other PNA's	0	2.2	6,480	624.480	22,500	200,000	200	29,700	200
n-Hexane	0	96	11,830	0	0	0	0	*i*	0
Other Alkanes	400,000	998,956	204,110	190,800	701,560	45,000	999,798	948,780	999,798
Olefins	600,000	930	170,740	36,750	50,000	0	*i*	*i*	
Cycloalkanes	0	11	68,880	41,200	150,000	5,000	*i*	*i*	
Other Compounds Indicated Present	Thiols		Pyridines Thiols Sulfides Quinolines	Phenols Carbonyls Pyridines Thiols Sulfides Quinolines	Pyridines Carbonyls Thiols Sulfides Quinolines				

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[a] Compositions are estimated to 2 or 3 significant figures. Additional significant figures are a result of calculational procedures, and they should not be given any importance.

[b] The symbol *i* means that the component has been indicated to be present, but the exact concentration is unknown.

The stream breakdown is combined with the stream analyses to get a component analysis of unit emissions. An example of this process is shown for an estimate of fugitive emissions from an FCC unit in Table 8-7.

A similar operation was performed separately on relief valves, since they are not distributed uniformly across the streams. Relief valves are usually placed at the top of a fractionating column or reactor vessel, and, thus, are exposed primarily to lighter streams. Table 8-8 shows the allocation of relief valves for the Aromatics Fractionation unit. The number of relief valves in each stream service was totaled, and the stream analyses were applied to the emissions, as shown in Table 8-9. All relief valves in the model refinery were assumed to vent to the atmosphere.

Still a different procedure was required to characterize the hydrocarbons emitted from the API separators. Analyses were available for the inlet oil to the separator and for the recovered oil. A hydrocarbon material balance was made to estimate the composition of the evaporative emissions from the separator, as shown in Table 8-10. The available analyses showed only the aromatics components, so the balance of the oil was assumed to fall in the alkane family.

This material balance approach assumes that any component lost from the oil phase is lost as evaporative emissions. This neglects the slight solubility of certain components which could result in mass transfer to the water phase (or eventually even the sludge phase). Thus, this approach results in a conservatively high, worst case assumption of the emission rate of individual species from the API separators.

Summary of Hydrocarbon Species Emissions--The emissions of selected hydrocarbon species were calculated by the above methods. The results are summarized in Table 8-11. These figures represent only

TABLE 8-7. FLUID CATALYTIC CRACKING - FUGITIVE EMISSION CHARACTERIZATION

		Weighted Contribution of each Component to Unit Emissions, in ppmw													
Stream	% of Unit Fugitives Attributable to that Stream	Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Polynuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
Atmos. Gas Oil	1	0	0	0	0	1	0	0	0	2	0	9495	0	500	0
Fuel Gas	30	0	0	0	0	0	0	0	0	0	0	276000	18000	0	6000
LPG Olefins	23	0	0	0	0	0	0	0	0	0	0	92000	138000	0	0
Cracked Naphtha	45	1296	40401	9644	77153	109562	4928			2916	5324	91850	76833	30096	0
Lt. Cycle Gas Oil	1	0	0	0	6	267	590	103	102	6245	0	1906	368	412	0
Hvy. Cycle Gas Oil	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total		1296	40401	9644	77159	109830	5518	103	102	9163	5324	471251	233201	31008	6000
	Emiss. Rate lb/hr														
	59.8	.078	2.42	.577	4.61	6.57	.33	.006	.006	.548	.318	28.18	13.95	1.85	.359

TABLE 8-8. RELIEF VALVE DISTRIBUTION

Example: Aromatics Fractionation Unit

Total Relief Valves = 6

Steam	No. of Relief Valves
Benzene	4
Toluene	2
Xylenes	0

TABLE 8-9. RELIEF VALVE SUMMARY - FUGITIVE EMISSION CHARACTERIZATION

Total # Relief Valves in that Service	Stream	% of Unit Fugitives Attributable to that Stream	Weighted Contribution of each Component to Unit Emissions, in ppmw													
			Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Polynuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
(42)	H_2 Recycle Gas	22.5	0	0	0	0	0	0	0	0	0	0	146250	0	0	78750
(12)	Fuel Gas	6.5	0	0	0	0	0	0	0	0	0	0	59800	3900	0	1300
(58)	LPG	31.1	0	0	0	0	0	0	0	0	0	0	311000	0	0	0
(4)	LPG Olefins	2.2	0	0	0	0	0	0	0	0	0	0	8800	13200	0	0
(33)	S.R. Naphtha	17.6	45	461	156	286	2918	257	1	111	2637	6835	87932	0	74361	0
(13)	Cracked Naphtha	7.0	202	6285	1500	12002	17043	767	0	0	454	828	14288	11952	4682	0
(8)	Reformate	4.3	232	3341	1441	7349	13949	318	0	0	30	1032	15308	0	0	0
(2)	Extract	1.1	196	2824	1217	6210	528	1	0	0	1	1	21	0	0	0
(2)	Raffinate	1.1	1	8	3	17	25	1	0	0	1	693	10252	0	0	0
(4)	Benzene	2.2	21846	44	0	0	0	0	0	0	0	110	0	0	0	0
(2)	Toluene	1.1	11	10921	44	11	0	0	0	0	0	0	13	0	0	0
(4)	SO_2	2.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
(2)	Middle Distillate	1.1	0	0	0	1	9	1	0	0	61	0	9828	0	1100	0
	TOTALS	100.0	22533	23884	4361	25876	34472	1345	1	111	3184	9499	663492	29052	80143	80050
	Normalized Total		23040	24421	4459	26458	35247	1345	1	113	3256	9713	678416	29705	81946	81850

TABLE 8-10. ESTIMATED COMPOSITION OF INLET OIL, HYDROCARBON VAPOR, AND OUTLET OIL STREAMS AROUND AN API SEPARATOR

	Estimated Composition of Streams (Wt %)		
Component	Inlet Oil	Vapor From Separator	Outlet (Skimmed) Oil
Benzene	0.03	0.07	0.01
Toluene	0.22	0.22	0.22
Ethylbenzene	0.06	0.06	0.06
Xylenes	0.21	0.21	0.21
Alkylbenzenes	0.80	0.80	0.80
Naphthalene	0.29	0.29	0.29
Anthracene	0.04	0.04	0.04
Biphenyl	0.18	0.18	0.18
Polynuclear Aromatics (PNA's)	2.04	0.15	2.98
Alkanes	96.13	97.98	95.21
	100.00	100.00	100.00

Skimmed Oil Rate = 667 lb./1000 lb. inlet oil

Vapor Lost from Separator = 333 lb./1000 lb. inlet oil

TABLE 8-11. SUMMARY OF HYDROCARBON SPECIES EMISSIONS FROM FUGITIVE SOURCES

Component	Source							
	V, P, C, F, D, CT*		Relief Valves		API Separators		Totals	
	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr
Benzene	7,200	2.8	23,000	0.4	700	0.4	3,900	3.6
Toluene	21,000	8.2	24,000	0.4	2,200	1.1	11,000	9.7
Ethylbenzene	5,600	2.2	4,500	0.1	590	0.3	2,800	2.6
Xylenes	31,000	12.1	26,000	0.4	2,100	1.1	15,000	13.6
Other Alkylbenzenes	42,000	16.6	35,000	0.6	7,900	4.1	23,000	21.3
Naphthalene	1,700	0.7	1,400	0.02	2,900	1.5	2,400	2.2
Anthracene	20	0.01	1	0.0	390	0.2	220	0.2
Biphenyl	230	0.1	110	0.0	1,800	0.9	1,100	1.0
Other PNA's	7,700	3.0	3,300	0.05	1,500	0.8	4,200	3.9
n-Hexane	16,000	6.3	9,700	0.2	i**	i	7,100	6.5
Other Alkanes	654,000	255.9	678,000	11.3	980,000	502.4	840,000	769.6
Olefins	46,000	18.1	30,000	0.5	i	i	20,000	18.6
Cycloalkanes	135,000	52.9	82,000	1.4	i	i	59,000	54.3
Hydrogen	31,000	12.3	82,000	1.4	i	i	15,000	13.7
TOTALS		391.2		16.8		512.8		920.8

* Fugitive emissions from valves, pumps, compressors, flanges, drains, and cooling towers.

** Components marked with "i" are indicated present, but no quantifiable concentration data were available.

fugitive hydrocarbon emissions and not the point source emissions from sources such as process heaters and fluid catalytic cracking regeneration. The stack hydrocarbon emissions did not significantly affect any of the critical emission points for hydrocarbon species because of the effects of height of release and plume rise.

8.3 Atmospheric Dispersion Modeling

Ground level concentrations of the various pollutants can be estimated using any one of a large variety of computer modeling techniques. The choice of the model and the details of its application to the refinery model are discussed in the following sections.

8.3.1 Choice of the Dispersion Model

There were several guidelines considered in choosing a model. First it should be an established, well accepted model. It should have the capacity to handle a large number of both point sources and area sources. It must be able to give not only the total concentration of the pollutant at any given point, but also the relative contribution of each source to that total.

Although not alone in satisfying these requirements, the EPA guideline model RAM[133] is certainly the most well-known. It has been extensively used and, at the time of this study, was accepted by regulatory agencies for flat terrain modeling. There are two versions of RAM, the rural and urban versions. The urban version has slightly higher dispersion coefficients to account for the numerous heat sources typical of an urban environment. As with other unconstrained choices, the worst case was chosen, which means the rural version of RAM.

The RAM model was not calibrated in this study. Raw predictions were used in evaluating the refinery impact. The use of raw predictions can result in ambient concentrations that are overestimated by as much as a factor of two.

8.3.2 Application of the Dispersion Model to the Hypothetical Refinery

The RAM dispersion model[133] is capable of predicting a 1- to 24-hour average concentration of relatively unreactive pollutants. A maximum of 250 point and 100 area sources can be modeled. Concentrations are predicted at a maximum of 150 selected locations (receptors).

RAM uses Gaussian steady-state dispersion algorithms for areas where one wind vector for each hour is a good approximation. Concentrations are calculated hour by hour as if the atmosphere had achieved a steady-state condition.

Meteorological parameters utilized by the model include wind speed, wind direction, temperature, atmospheric stability class, and mixing height. The parameters are set by the "standard receiving atmosphere" as defined by Monsanto in their source severity work.[130] The worst case wind direction was determined by comparing the results of modeling for wind blowing for one hour from each of 16 different directions. After determining the worst case wind direction, a repeating sequence of 3 wind directions (1 hour from the worst case direction and 1 hour each from 5 degrees on either side of the worst case direction) was used to obtain mean concentrations for short averaging times. It is recognized that the persistance of these conditions for a 24-hour period is quite improbable. This assumption again results in a worst case approximation of "real world" conditions. The source severity methodology is specific in requiring that these conditions be used, and no provisions are given to incorporate variations when modeling for longer averaging times.

Annual concentrations (for comparison with NO_2 NAAQS) can be predicted with Larsen statistics.[134] Using empirically determined ratios, the maximum annual concentration can be determined from mean concentrations for shorter averaging times. These ratios are functions of the standard geometric means (SGM) of the shorter averaging times.

The dispersion coefficients are empirically-determined as functions of atmospheric turbulence, distance from the source and the concentration averaging time. Thus, the spread of the plume is dependent on these three factors. The atmospheric turbulence is defined by stability classes. These classes, which range from very unstable to neutral to very stable atmospheres, are determined by wind speed and insolation during the day, or wind speed and cloud cover during the night. The most unstable class is A. Class F the most stable. The C stability class used here is considered neutral.[135]

RAM can accept both point source and area source inputs. The data required to characterize a point source includes source coordinate, emission rate, physical height, stack diameter, stack gas exit velocity, and stack gas temperature. Area source parameters consist of coordinates of the southwest corner, side length, total area emission rate, and effective height.

Stacks, flares, etc., were modeled as point sources. Fugitive emissions were modeled by three different methods.

(1) As a single point source originating in the center of the process unit plot.

(2) As a pseudo-area source (where the single point source was divided into three point sources distributed across the unit in a plane perpendicular to the worst-case wind direction).

(3) As area sources.

The point source approach gave very unrealistic boundary line conditions with large concentration peaks directly downwind of the unit centerlines and very low concentrations elsewhere. The pseudo-area approach had some smoothing effect, but only the rigorous area source approach gave satisfactory results.

Concentrations from the point sources are a function of the distance downwind and crosswind from the source to the receptor. Concentrations due to area sources are calculated using the narrow plume approximation. This neglects diffusion in the crosswind direction and assumes that an area source consists of many narrow plumed point sources. As a result, any receptor that has no area sources directly upwind receives no contribution to its predicted concentration from area sources. This approximation is good when modeling large urban area sources.[136] The five degree variation in wind persistence did add some dispersion outside the worst-case wind direction streamline.

The locations of a series of permanent receptor sites were also input to the model. The locations consisted of a grid placed in the area of greatest impact as predicted by the worst case wind direction. The model then calculated the 24-hour average concentration at each receptor. From these data, maximum concentrations were determined. Also, isopleths (lines of equal concentration) were plotted. Not only were the total ambient concentrations displayed for each receptor, but these concentrations were broken up into their component contributions from each of the sources.

8.4 Impacts on Ambient Air Quality

8.4.1 Criteria Pollutants and Total Hydrocarbons

The modeling results for criteria pollutants and total hydrocarbons are summarized in Table 8-12. Four of the predicted pollutant concentrations do not exceed the NAAQS, those being particulates, oxides of sulfur, oxides of nitrogen, and carbon monoxide. The maximum ground level concentration of particulates was 68 $\mu g/m^3$ as compared to the NAAQS of 260 $\mu g/m^3$. These values include only process particulates which result primarily from the FCC and oil fired heaters, and do not include fugitive dust from unpaved roads, construction activities, or coke handling. The point of maximum concentration occurred due west of the refinery center at a distance of 1.5 kilometers from the fence line.

The maximum concentrations of SO_x was found to be 233 $\mu g/m^3$ as compared to the NAAQS of 365 $\mu g/m^3$. The maximum point was due west of the sulfur recovery complex and occurred at one-half kilometer from the refinery boundary.

The maximum 1-hour concentration of CO was predicted to be 17 $\mu g/m^3$ as compared to an NAAQS of 10,000 $\mu g/m^3$. The maximum point occurred due west of the refinery center and at a distance of 1.25 kilometers from the boundary line.

The maximum 24-hour average NO_2 concentration was estimated to be 269 $\mu g/m^3$. By applying Larsen statistics as discussed in Appendix D (Volume 4), the predicted annual average NO_2 concentration at the point of maximum concentration was estimated to be 55 $\mu g/m^3$. This figure is well below the NAAQS value of 100 $\mu g/m^3$ as a maximum annual average. This predictive estimate has been based on the assumption that all of the NO_x is emitted as NO_2. Actual NO_2 concentrations are likely to be significantly lower than the predicted value.

TABLE 8-12. SOURCE SEVERITY FACTORS FOR CRITERIA POLLUTANTS

Pollutant	$\overline{X}_{max}$[†] μg/m³	F[††] μg/m³	S[†††]
Particulates	68	260	0.26
SO_2	288	365	0.78
CO	16	10,000	0.0016
NO_2	55	100	0.55
Nonmethane hydrocarbons*	9644	160	60.3

[†] $\overline{X}_{max}$ is the maximum ground level concentration.

[††] F is the acceptable pollutant concentration (which is the NAAQS for criteria pollutants).

[†††] S is the source severity, with the following decision levels.

if $S \geq 1$: Additional Emission Reduction Probably Required

if $0.1^{**} \leq S < 1.0$: May or May Not Require Additional Emission Reduction

if $S < 0.1^{**}$: Additional Emission Reduction Probably Not Required

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* The nonmethane hydrocarbon standard is a guideline standard based on the estimated contributions of hydrocarbons to oxidant formation.

** The lower critical value may need to be as low as 0.01 where large uncertainties are involved.

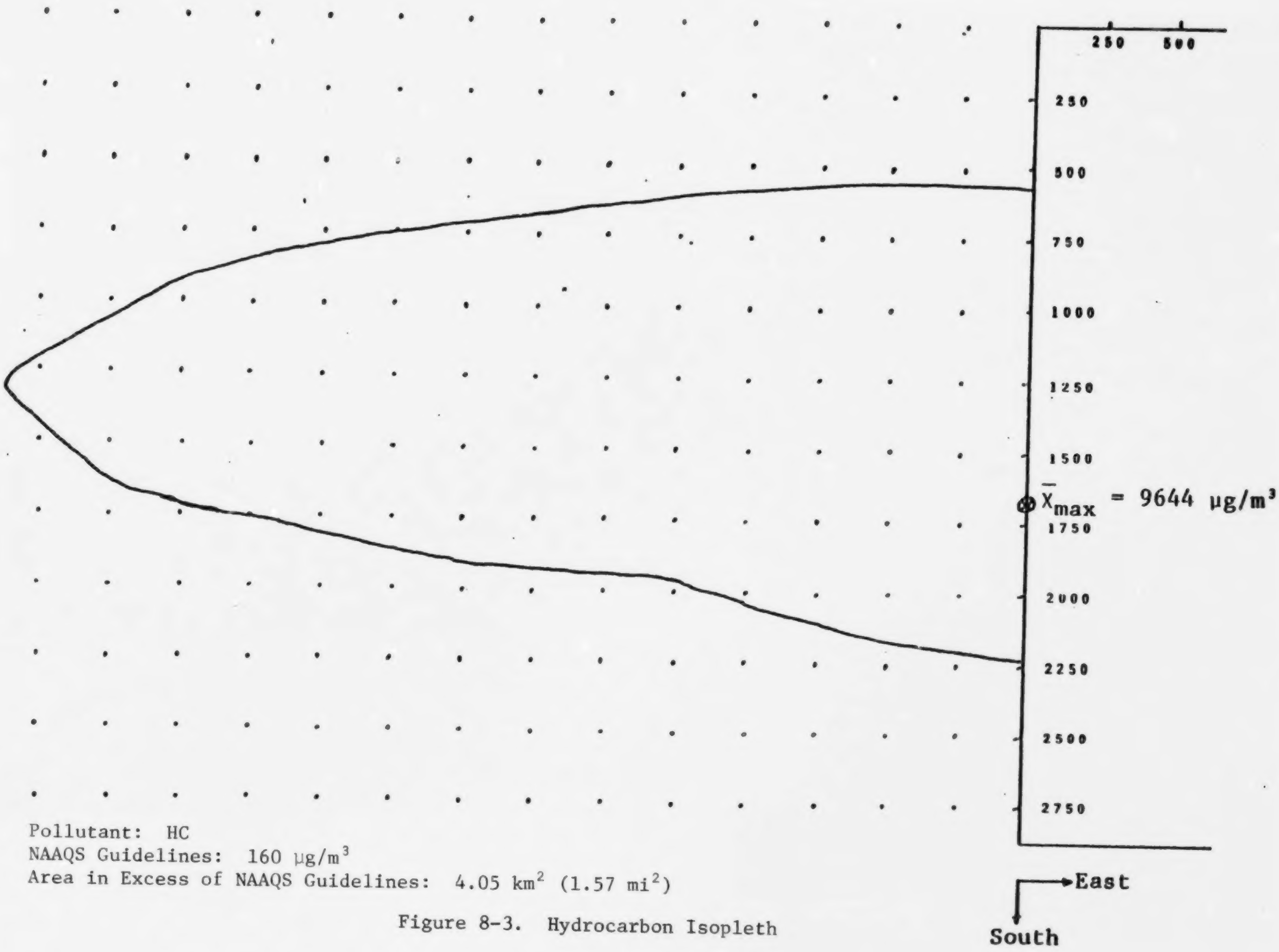
An analysis of the source severity factors indicates that none of the criteria pollutants has a high probability of causing a public hazard (as indicated by $S > 1$). On the other hand, only CO has a source severity factor low enough to have confidence that it does not create a hazard. The others are in the area of uncertainty where no clear decision can be made.

The total hydrocarbon concentration was found to exceed the federal guideline for 3-hour maximum (6-9 AM) nonmethane hydrocarbon concentration of 160 $\mu g/m^3$, with a maximum concentration of 9644 $\mu g/m^3$. The point of maximum concentration was located on the refinery boundary, due west of the main processing area. Although the concentrations fell off rapidly from the maximum, the 160 $\mu g/m^3$ isopleth extends about 3.5 kilometers downwind and encompasses about four square kilometers, as shown in Figure 8-3. The source severity factor for total hydrocarbons is quite high. However, the NAAQS guideline for hydrocarbons is based on the prevention of the formation of photochemical oxidants rather than on primary toxicity data. It should be noted that this guideline is no longer widely accepted or used because the relationship between ozone formation and ambient hydrocarbon concentrations is not adequately defined.

8.4.2 Selected Hydrocarbon Components

The ambient concentration of any given hydrocarbon species can be determined by summing the contribution of the component from all modeled sources. The RAM model is capable of performing this analysis with the assumption that all species will disperse at the same rate; that is, atmospheric turbulence outweighs any differences in molecular diffusion between species.

The first point of interest is the receptor showing the largest total hydrocarbon concentration. Table 8-13 shows the component breakdown at that point. This maximum point is located directly downwind of the API



Pollutant: HC
NAAQS Guidelines: 160 µg/m³
Area in Excess of NAAQS Guidelines: 4.05 km² (1.57 mi²)

Figure 8-3. Hydrocarbon Isopleth

TABLE 8-13. HYDROCARBON SPECIES AMBIENT CONCENTRATION AT THE POINT OF MAXIMUM TOTAL HYDROCARBON CONCENTRATION

Location: On the west boundary line at a point 1650 meters from the northwest corner; directly downwind of source L49 (an API separator).

Component	Concentration, $\mu g/m^3$	Concentration, ppmv
Benzene	6.6	0.0019
Toluene	21.2	0.0051
Ethylbenzene	5.7	0.0012
Xylenes	19.8	0.004
Other Alkylbenzenes	102.2	0.017
Naphthalene	27.5	0.0047
Anthracene	3.6	0.0005
Biphenyl	16.5	0.0025
Other Polynuclear Aromatics	22.7	0.0030
n-Hexane	2.8	0.0007
Other Alkanes	9380.0	1.876
Olefins	0.0	0.0
Cycloalkanes	33.7	0.009
H_2	1.8	0.020
Total Hydrocarbons	9644.0 $\mu g/m^3$	1.95 ppmv

separator (Source L-49), and 97.8 percent of the hydrocarbon species at that point came from the separator. The bulk of the hydrocarbons are from the alkane family (9380 $\mu g/m^3$ or 1.9 ppmv), but both the aromatics and polynuclear aromatics species are present at the part per billion level (PPB).

It is also desirable to find the point of maximum concentration for each hazardous component. A limited search was carried out to find these species maximum points by finding the maximum points for units with high concentrations of the subject species. Resulting maximum concentrations are summarized in Table 8-14.

All of the species maximum concentrations were found at the two points having the highest concentration of total hydrocarbons. Five species (including benzene, naphthalene, anthracene, biphenyl, and the general polynuclear aromatics family) had maximum concentrations adjacent to the API separator. The maximum concentrations of other species were found at a receptor on the west boundary about 1380 meters from the northwest corner. The largest contributor to this point was the crude distillation unit (L28-1). Other significant contributing units included the two catalytic reformers (L36-1 and 29-1), aromatics extraction (L37-1), alkylation (L32-1), fluid catalytic cracking (L38-1), delayed coking (L40-1), hydrogen plant (L31-1), and resid hydrodesulfurization (L30-1). The largest concentration for any single component examined was found to be hexane at a concentration of 15 ppbv.

To assess the impact of a given concentration of a pollutant species, quantifiable toxicity data must be available. The Monsanto approach uses the term "acceptable pollutant concentration" as the level at which there is a very low probability of adverse impacts on the general public. For criteria pollutants, the Primary Ambient Air Quality Standards (PAAQS) were used as the acceptable pollutant concentrations.

TABLE 8-14. MAXIMUM AMBIENT CONCENTRATION OF SELECTED HYDROCARBON SPECIES

Component	Ambient Concentration		Location
	$\mu g/m^3$	ppmv	On the West Boundary, XXXX meters from the Northwest Corner
Benzene	6.6	0.0019	1650
Toluene	26.3	0.0063	1380
Ethylbenzene	10.7	0.0022	1380
Xylenes	53.6	0.0092	1380
Other Alkylbenzenes	105.5	0.0179	1380
Naphthalene	27.5	0.0047	1650
Anthracene	3.6	0.0005	1650
Biphenyl	16.5	0.0025	1650
Other Polynuclear Aromatics	22.7	0.0030	1650
n-Hexane	58.5	0.0152	1380
Olefins	37.6	0.010	1380
Cycloalkanes	365.8	0.099	1380

For other species, the acceptable concentration can be defined from the Threshold Limit Value (TLV) as shown below:

$$F = TLV(G)$$

where

$$G = (8/24)\ (1/100) = 1/300,$$

so

$$F = TLV/300.$$

The factor "G" is defined as a conversion factor to express TLV values as "equivalent PAAQS." G is defined as 1/300. This comes from two factors:

- The ratio (8/24) converts the TLV from an 8-hour per day basis to a 24-hour basis.
- The factor (1/100) is a safety factor to account for the fact that the general public is more susceptible to illness than the industrial work force (for whom the TLV was set).

Table 8-15 shows a summary of the acceptable pollutant concentrations that result from this operation. The values in parentheses are values arbitrarily assigned to a family of chemicals, some of whose members have TLV's that average out to the assigned value. These values should be used with caution. Not all of the members of such a family are equally toxic, nor is it certain that their effects would be additive. If the source severity factors based on these values are low, then it can be said with some confidence that no damage will be done by those compounds. If the values are high, however, no conclusions can be drawn.

TABLE 8-15. SUMMARY OF "F" VALUES

Pollutant	F μg/m^3	Based on
Benzene	114	TLV = 10 PPM
Toluene	1,388	TLV = 100 PPM
Ethylbenzene	1,586	TLV = 100 PPM
Xylenes	1,586	TLV = 100 PPM
Other Alkylbenzenes	(488)**	TLV = (25 PPM)
Naphthalene	194	TLV = 10 PPM
Anthracene	0.66	TLV = 200 μg/m^3*
Biphenyl	4.4	TLV = 0.2 PPM
Other Polynuclear Aromatics	(25)	TLV = (1 PPM)
n-Hexane	1,281	TLV = 100 PPM
Other Alkanes	(16,665)	TLV = (1,000 PPM)
Olefins	(12,344)	TLV = (1,000 PPM)
Cyloalkanes	(4,937)	TLV = (400 PPM)

* Based on "Coal Tar Pitch Volatiles" which anthracene is a major component.

** TLV values arbitrarily assigned to a family of chemicals.

The whole process of basing an acceptable pollutant concentration on TLV's should be critically appraised. These values were set for use in industrial hygiene studies within plant boundaries, and the American Conference of Governmental Industrial Hygienists (ACGIH) specifically warns against their use:

- as a relative index of hazard or toxicity,
- in the evaluation of community air pollution, or
- in estimating the toxic potential of continuous, uninterrupted exposure.

While such usage is discouraged, the fact remains that no other source of quantifiable toxicity levels is available. Therefore, the use of TLV's to estimate acceptable pollutant concentrations is used here in accordance with the source severity methodology. It is felt that this comparison, however tenuous it might be, is better than ignoring the problem. This is especially true as long as the proper qualifications and limitations on the results are explicitly stated.

Taking the maximum ambient concentrations presented in Table 8-14 and the acceptable pollutant concentrations shown in Table 8-15, it is straightforward to calculate source severity factors for each component. These factors are shown in Table 8-16.

Using Monsanto's recommended decision levels, it can be said that there is a significant probability that anthracene and biphenyl need further application of control technology. Several things should be noted in the context:

- The high concentrations of these species were contributed by a covered API separator.

TABLE 8-16. SOURCE SEVERITY FACTORS FOR SELECTED HYDROCARBON SPECIES

Component	$\overline{X}_{max}$ µg/m^3	F µg/m^3	S
Benzene	6.6	114	0.06
Toluene	26.3	1388	0.02
Ethylbenzene	10.7	1586	0.007
Xylenes	53.6	1586	0.03
Other Alkylbenzenes	105.5	(488)*	(0.22)
Naphthalene	27.5	194	0.14
Anthracene	3.6	(0.66)	(5.5)
Biphenyl	16.5	4.4	3.8
Other Polynuclear Aromatics	22.7	(25)	(0.9)
n-Hexane	58.5	1281	0.05
Olefins	37.6	(12344)	(0.003)
Cycloalkanes	365.8	(4937)	(0.07)

*Values in parentheses are an average of the F values for several selected members of the family group, and are not true F values for the entire family.

- That separator was located right on the plant boundary line, which is quite unusual.

- There is a great deal of uncertainty in the emission factor for separators. No conclusive results were obtained from limited testing of separators on this program, so AP-42[7] factors were used in this analysis. The EPA has since begun a program to improve these factors.

- The emissions from an API separator are highly variable in component breakdown (much more so than process unit emissions), and the species breakdown for that unit is based on several grab samples which may well not be reflective of "typical" operation.

- These component emissions (calculated by an oil-phase volatile hydrocarbon balance) may be overstated due to solubility effects.

It can also be stated that there is a very low probability of the need for further control of ethylbenzene and the olefin family. All other species fall into the range where no clear decision can be made. The uncertainties involved in the calculation of these source severity factors make it impossible to make clean cut decisions for the range from 0.01 to 0.99.

It should also be noted here that all of the quoted hydrocarbon species maximum points occurred on the refinery boundary. Because they are released close to the ground and with little velocity or thermal buoyancy, the vapors tend to stay at ground level. Dispersion does proceed at a relatively rapid pace when moving downwind. This establishes two interesting points:

- The sphere of influence for hydrocarbon species that were noted as potential problems at the boundary line does not extend more than a few hundred meters.

- This further suggests that buffering areas with a high potential for fugitive emissions could be effective in reducing or eliminating high source severities.

8.4.3 Discussion of Results

The sensitivity of the source severity values to a number of variables was estimated. The most significant variables include refinery processing configuration, refinery layout, calculated emissions, type of atmospheric dispersion model, meteorological conditions, hydrocarbon component breakdown, and toxicity values.

Several of these variables can be considered in a group. A change in the calculated emission rates will produce a proportional change in the predicted maximum concentrations. These emissions will vary with a change in refinery processing configuration, emission factors, or fitting count.

Another point of uncertainty is the potential contribution of storage emissions to the impacts predicted for the refinery process area. Total storage tank emissions were estimated to contribute about 27 percent of all nonmethane hydrocarbon emissions. Since no layout information within the module was available, each storage module was treated as an area source. The specific emission rates ($lb/hr/ft^2$) were calculated for each module and compared to the API separator and the process area which contributed to the two highest points of nonmethane hydrocarbon concentration. The following conclusions can be drawn:

- The worst storage tank module (L-22) had a specific emission rate of 85.4 $lb/hr/10^6\ ft^2$. This figure is much lower than either the covered API separator (L-49) with 1169 $lb/hr/10^6\ ft^2$ or the worst process area (near L-28) with 320 $lb/hr/10^6\ ft^2$.

- Since all of these sources are directly adjacent to the west boundary line, the predicted impacts should be roughly proportional to the specific emission rates. This is actually somewhat conservative, since the height of release of the storage tank emissions would be considerably higher than for a separator or for process fugitives. Therefore, it can be concluded that the specific impact of the worst storage module would be significantly less severe than the two worst points cited in this assessment.

- By examining the relative contributions of adjacent process sources to the predicted maximum and applying similar ratios to adjacent storage modules, it was determined that the inclusion of storage emissions in the modeling would not have significantly increased the estimated maximum concentration. It would, however, have greatly increased the area of impact in which relatively high concentrations of nonmethane hydrocarbons would occur.

The refinery layout may be even more critical than the complexity and the resulting overall emission rate, especially for the predicted hydrocarbon species. Fugitive emissions are released near ground level, and, thus, are subject to much less dispersion than stack emissions. A refinery layout with process units right on the boundary line (such as the model used here) will show much higher hydrocarbon concentrations outside the refinery boundaries than one with a buffer zone around the processing area.

The choice of dispersion model type could affect the predicted pollutant concentrations significantly. None of the available models is perfect, and predicted maximum concentrations may vary from half to ten times (or more) the actual concentrations measured from a source. The use of the rural version of RAM to model a refinery is a conservative choice since the heat island effect of a refinery will tend to increase atmospheric diffusion.

The predicted impacts will vary with meteorological conditions as illustrated by sensitivity runs on the model. A 22 percent decrease in wind speed resulted in a 28 percent increase in predicted maximum ground level concentrations for total hydrocarbons. Use of the more stable atmospheric stability class D resulted in 3 percent higher predicted concentrations.

The hydrocarbon component breakdown is quite critical. Individual component source severity factors will vary in direct proportion with the predicted concentration of that component in the emitting source. There are fairly wide confidence intervals that should be applied to those component breakdowns. Component concentrations will vary from day to day with changes in such things as feedstocks and operating conditions. This effect is amplified by several orders of magnitude when discussing API separator emissions. The small number of samples on which the component analyses are based is insufficient to confidently average out such process variations.

There is a shortage of quantifiable toxicity data for the many organic compounds present in refinery processing. This makes it difficult to prepare a comprehensive environmental assessment. The accuracy of existing toxicity data is also questionable, and this effect is compounded by the transformation from TLV to an "acceptable pollutant concentration." Dividing the TLV by three to account for the difference between eight hours per day and continuous exposure assumes that the toxic effects are cumulative. For some compounds that is certainly true, but others require some critical concentration to be harmful and are easily assimilated by the body below that concentration. The safety factor of one hundred used to account for the greater susceptibility of the general public is obviously arbitrary and therefore questionable. Any of these changes in the acceptable pollutant concentration will produce an inversely proportional change in the calculated source severity.

Recognizing the high degree of uncertainty in the results, the following conclusions can be drawn:

- There is no certainty of public hazard resulting from the emissions of this hypothetical refinery.
- Conversely, there is no certainty that it does not create a hazard.
- If any hazard exists due to hydrocarbon species, the most likely species to cause problems would be the polynuclear aromatics.
- This approach to an environmental assessment of a generalized source is of limited value in providing specific information on whether steps need to be taken to further reduce emissions of a given pollutant.
- The results can be useful in indicating the relative impacts of various emission sources and species. For instance, API separators appear to pose more of a potential hazard than fluid catalytic crackers; polynuclear aromatics emissions appear to be more troublesome than benzene. Such relative ranking of emission sources and species can be useful in directing emphasis towards potential problem areas.

- If this approach were used to assess the impact of a specific plant, it might yield more useful results. The range of uncertainty would be much narrower because the input factors could be more firmly defined.

8.5 Effects of Existing and Potential Regulations and Policies

This section contains an examination of the effects of environmental regulations and permit policies on the emissions from petroleum refining. The first two subsections deal with state and federal regulations, respectively. The final section addresses the effects of potential new regulations.

8.5.1 State Regulations

Existing refineries are regulated by the states, rather than by federal standards. Standards for the South Coast and Bay Area regions of California are considered here with the state regulations. Though some state regulations were amended as late as 1979, most were adopted in the early 1970's.

There is disparity among the regulations in some categories; the general trends which could be discerned are presented here along with notable exceptions. No attempt is made to describe the regulations of the individual states *per se*.

All states are included even if they presently have no refineries. This should *not* be interpreted, however, to mean that all states have specific regulations for all the pollutant categories included here. Some states have regulations only for specific existing facilities; others have no regulations except those supporting federal standards.

Particulate and Visible Emissions--Most states have specific standards for the maximum opacity and darkness of emissions. The strictest standard, and by far the most common, calls for a maximum opacity of 20 percent and a maximum darkness of No. 1 on the Ringlemann Chart. In some states these stricter standards apply only to new sources, while existing sources are allowed an opacity of 40 percent and a darkness of No. 2 Ringlemann. In other states these more lenient standards apply to new and existing sources. One state allows 40 percent opacity for new sources and 60 percent for existing sources.

Some state standards specify either opacity or darkness, but not both. Exception to the above standards is sometimes allowed for the flue gases from catalytic cracking catalyst regeneration and fluid coking: these gases may be allowed 25 to 40 percent opacity where other gases are limited to 20 percent. In all states with visibility standards, provision is made for varying amounts of upset time.

Particulates are generally regulated by source. For process emissions in general, many state regulations incorporate a chart with pounds per hour allowable emissions versus tons per hour process weight, with all stacks being considered collectively.

Again, catalytic cracking catalyst regeneration is sometimes considered separately, although no exact comparison of the various regulations can be made because of widely varying formats. A one pound per ton of coke burn-off regulation found in two states appears to be the most stringent. When a CO boiler is installed on the regenerator, an allowance is usually made for the added emissions from fuel-burning.

Particulate emissions from fuel-burning are also often considered separately. The stipulation is generally made that all fuel-burning at the facility is considered collectively. Regulations range from 0.1 to 2.5 pounds of particulates per million Btu of heat input; many of the regulations stipulate a maximum of 0.6 lb/10^6 Btu or less. Some regulations have varying maximums for different size units. One state regulation specifies that afterburners must be used.

Sulfur Emissions--Several states limit SO_2 emissions from any source in a refinery to 500 ppmv; a common maximum is 2000 ppmv. One state limits total SO_2 emissions from the refinery to 10 percent of the sulfur in the crude; another limits total SO_2 emissions to 0.3 pounds per barrel of oil processed. Many states, however, consider separately the sulfur emissions from fuel burning and sulfur recovery. One state limits emissions of mercaptans specifically to 0.25 pounds per hour.

Most regulations for SO_2 emissions from fuel burning are of two types. Some states limit the sulfur content of the fuel burned while others specify a maximum amount of SO_2 that may be emitted per million Btu of heat input. When the sulfur content of the fuel is limited, allowance is usually made for equivalent alternate means of SO_2 emission control.

Where the sulfur content of the fuel is limited, state regulations stipulate maximums of up to 2.5 weight percent sulfur. Most maximums are 1.0 weight percent sulfur or less. Sulfur content of gaseous fuels (often specifically fuel gas) is expressed in grains of H_2S per dry standard cubic fool (gr/dscf). In this case the common maximum is 0.1 gr/dscf.

Allowable SO_2 emissions from sulfur recovery units are sometimes expressed in pounds of SO_2 per pound of sulfur processed. These allowances range from 0.004 to 0.12 lb SO_2/lb S. Several state regulations contain a chart of allowable emissions versus sulfur input. One state allows up to 1000 pounds of SO_2 per hour. Limits of 500 to 2000 ppmv SO_2 are in some instances set specifically for sulfur recovery units.

Hydrogen sulfide emissions from sulfur recovery units are addressed by a few states. One state allows 0.3 pounds of H_2S per hour. One state allows 0.1 ppm H_2S and two others allow 10 ppm H_2S.

NO_x Emissions--State regulations for the control of NO_x emissions from fuel burning are quite consistent. These regulations, which normally apply only to units larger than 250 million Btu, allow gas-fueled units to emit 0.20 pounds per million Btu and liquid-fueled units to emit 0.3 pounds per million Btu. Solid-fueled units are allowed 0.7 pounds per million Btu. When different fuels are burned simultaneously, the applicable regulation is determined by proration.

Carbon Monoxide Emissions--One state limits carbon monoxide to 200 ppmv in fuel-burning units larger than 10^7 Btu. All other CO regulations are for catalytic cracking catalyst regeneration and for fluid coking. Some states limit CO emissions from these sources to 500 ppmv; in some instances this limit applies only to new sources. One state allows existing sources to emit 20,000 ppmv CO; another allows the emission of 5 tons of CO per year.

The control method for CO emissions from catalyst regeneration and fluid coking is expressed specifically in several regulations as combustion at 1300°F for 0.3 second in a direct flame afterburner or boiler with an indicating pyrometer located at eye level. Some, but not all, states with this stipulation allow the use of equivalent control measures. One state allows alternative control methods which remove at least 93 percent of the CO in the exiting gas.

Hydrocarbon Emissions--Some regulations stipulate that oil-water separators must be pressurized, have floating or double-deck roofs, have vapor recovery, or have an equivalent vapor control method. One state regulation specified 85 percent control for wastewater separators, another 95 percent.

Most standards for pumps and compressors state simply that these must be equipped with mechanical seals or an equivalent control. Several states specify mechanical seals for rotating pumps and compressors and packing glands for reciprocating. Two states limit emissions from each pump and compressor to 2 cubic inches of liquid per 15 minutes; one limits leakage to 3 drops per minute.

A number of states specify that hydrocarbon waste from the vapor blowdown system be smokelessly flared or disposed of in an equivalent manner. One state specifies that these emissions be controlled if they are more than 10 percent equivalent methane; another state sets a limit of 50 pounds per day.

Hydrocarbon emissions from catalytic crackers and fluid cokers are required by several states to be incinerated in a direct flame afterburner or boiler. One state allows 100 ppm equivalent methane or 8 pounds of hydrocarbons per hour before controls must be applied; another state allows 5 tons of hydrocarbons per year.

Other sources of hydrocarbon emissions are mentioned infrequently in state regulations. Several regulations specify that hydrocarbon emissions from condensers, hot wells and accumulators be incinerated, compressed, or equivalently controlled. One standard allows no hydrocarbon emissions from fuel burning; another specifies 95 percent control of hydrocarbons from vacuum systems and from process unit turnarounds. One regulation states that relief valves in pipes over one inch in diameter must be vented to vapor recovery or disposal, be protected by a rupture disc, or be maintained by an approved inspection system. In one regulation, emissions from air blowing must be incinerated at 1400°F for 0.3 second or equivalently controlled.

Effects of State Regulations on the Environmental Impacts of Refineries--It is difficult to assess the effects of state regulations because of this great variety. There is no doubt that significant emission reductions have been achieved over the last ten to fifteen years by virtue of these regulations. The model refinery used in this environmental assessment, however, already reflects the control technology required by the consensus of regulations for existing sources. Some reduction of the impacts could be expected if the refinery was located in one of the stricter states.

8.5.2 Federal Regulations and Policies

Federal regulations apply primarily to new or modified sources. These take the form of New Source Performance Standards (NSPS) and New Source Reviews required for permitting.

New Source Performance Standards--NSPS specific to refineries are contained in 40 CFR Part 60, Subpart J. These standards apply to fluid catalytic cracking unit regenerators, fluid cokers, sulfur recovery units, and fuel sulfur levels. Subpart D contains standards for fossil-fuel fired steam generators with a heat input greater than 250 million Btu. Subpart K includes standards for storage vessels containing petroleum liquids, but these are outside the scope of this study.

Particulate and Visible Emissions--Federal standards state that gases from fossil-fuel fired steam generators may not exhibit more than 20 percent opacity except for one 20-minute period per hour of not more than 27 percent opacity. These gases also may not contain more than 0.1 pound of particulate matter per million Btu of heat input from the fossil-fuel.

Gases from fluid catalytic cracking catalyst regeneration may not exhibit more than 30 percent opacity, except for one six-minute average reading per hour. These gases also may not contain more than 1.0 pound of particulate matter per 1000 pounds of coke burn off.

If the gases from the regenerator pass through an incinerator or waste heat boiler in which auxiliary or supplemental liquid or solid fuel is burned, excess particulate emissions may be allowed. These excess emissions may be 0.1 pound or less per million Btu of heat input attributable to the added fuel.

Sulfur Emissions--When liquid fuels are used for steam generation, sulfur dioxide emissions must be no more than 0.8 pounds per million Btu of heat input. Any fuel gas which is burned in a combustion device must contain no more than 0.10 grain of H_2S per dry standard cubic foot or the sulfur dioxide emissions from the combustion device must be controlled in an equivalent manner. Flares for the combustion of process upset gas or fuel gas from relief valve leakage are exempt from this standard. Sulfur dioxide emissions from Claus plants must be limited to 0.025 percent (250 ppm) by volume on a dry basis at zero percent oxygen if emissions are controlled by an oxidation system (one which converts emissions to hydrogen sulfide) followed by incineration. If emissions are controlled by a reduction system not followed by incineration, emissions from the unit may be 0.030 percent (300 ppm) reduced sulfur compounds and 0.0010 percent (10 ppm) hydrogen sulfide calculated as sulfur dioxide at zero percent oxygen on a dry basis. Reduced sulfur compounds include hydrogen sulfide, carbonyl sulfide, and carbon disulfide.

Carbon Monoxide Emissions--The standards for carbon monoxide states simply that no gases which contain more than 0.050 percent by volume (500 ppmv) carbon monoxide may be discharged to the atmosphere from a fluid catalytic cracking catalyst regenerator.

NO_x Emissions--Allowable NO_x emissions from fossil-fueled steam generators vary with the type of fuel used. When gaseous fuel is used, emissions are limited to 0.2 pounds per million Btu of heat input. For liquid fuels the limit is 0.3 $lb/10^6$ Btu and for solid fuels 0.7 $lb/10^6$ Btu.

When different fuels are burned simultaneously, the applicable standard is determined by proration.

New Source Review--The 1977 Amendments to the Clean Air Act emphasize the control of atmospheric pollutants from new or modified facilities by establishing a New Source Review (NSR) process. This is essentially a federal permit to construct any major emission source. The review process can take one of two paths depending on whether or not the source is to be built in an area in attainment of the National Ambient Air Quality Standards (NAAQS). If so, the Prevention of Significant Deterioration (PSD) regulations apply. If not, then nonattainment regulations apply. Frequently both paths must be followed, since attainment is judged on a pollutant-by-pollutant basis.

Prevention of Significant Deterioration--The PSD review process is a multilevel examination of the emission levels and air impacts of the new source. The overall process can best be illustrated by the flowchart shown in Figure 8-4. It would not be pertinent here to examine in detail the many applicability criteria which determine the level of review required. Suffice it to say that if a new or modified refinery (which is one of the 28 major industry categories) has the potential to emit more than 100 tons per year of any given atmospheric pollutant, and that represents a net increase in emissions since 8/7/77, the new or modified section must demonstrate the use of Best Available Control Technology (BACT).

BACT is defined as the level of emission control which gives the lowest emissions while taking into consideration the cost of control, energy efficiency, and technical feasibility. BACT must, therefore, be determined on a case-by-case basis to evaluate these effects. When an NSPS is available, this usually forms the minimum criteria for BACT. When no NSPS exists, then all possible methods of emission reduction must be catalogued. When one of these methods has been proposed as BACT for the

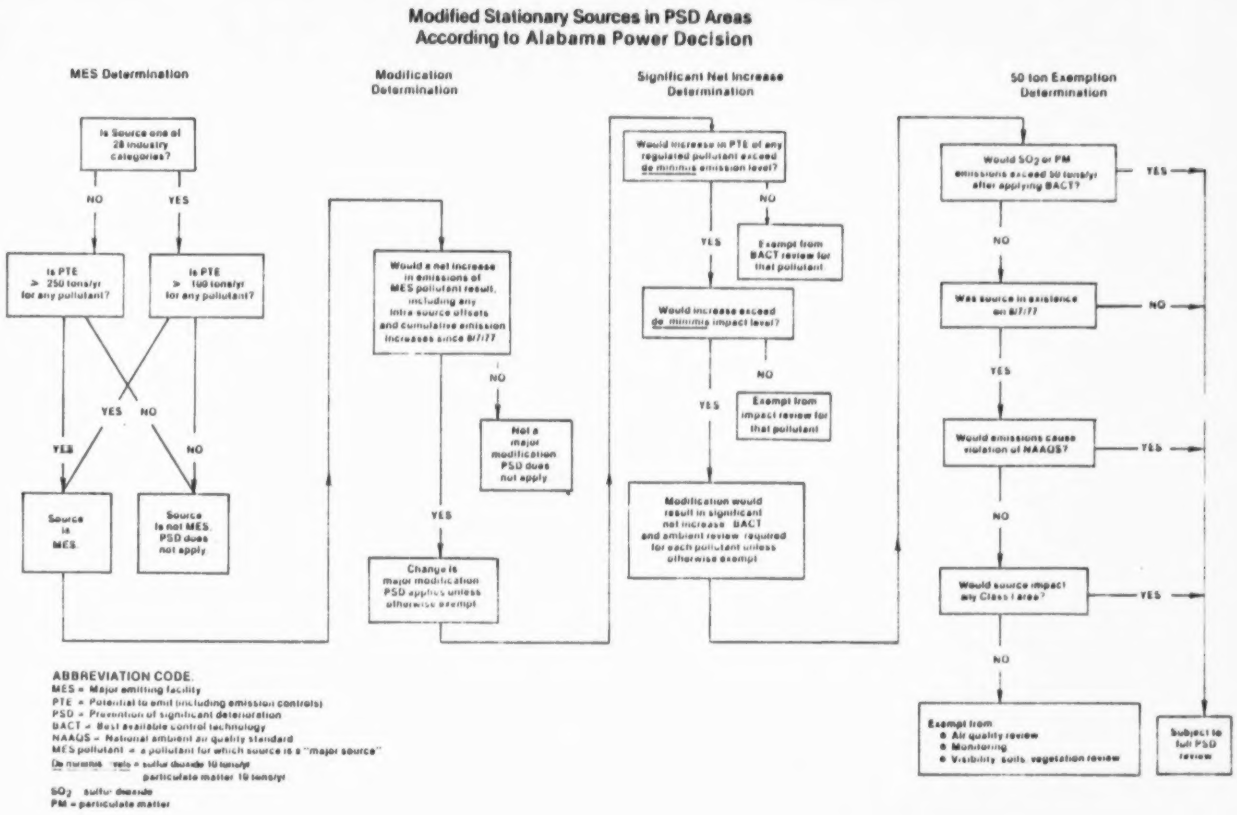

Modified Stationary Sources in PSD Areas
According to Alabama Power Decision
MES Determination
Modification Determination
Significant Net Increase Determination
50 ton Exemption Determination
Is Source one of 28 industry categories?
NO
YES
Is PTE > 250 tons/yr for any pollutant?
Is PTE > 100 tons/yr for any pollutant?
YES
NO
YES
NO
Source is MES.
Source is not MES. PSD does not apply.
Would a net increase in emissions of MES pollutant result, including any intra source offsets and cumulative emission increases since 8/7/77
NO
Not a major modification PSD does not apply
YES
Change is major modification PSD applies unless otherwise exempt
Would increase in PTE of any regulated pollutant exceed de minimis emission level?
NO
Exempt from BACT review for that pollutant
YES
Would increase exceed de minimis impact level?
NO
Exempt from impact review for that pollutant
YES
Modification would result in significant net increase. BACT and ambient review required for each pollutant unless otherwise exempt
Would SO_2 or PM emissions exceed 50 tons/yr after applying BACT?
YES
NO
Was source in existence on 8/7/77
NO
YES
Would emissions cause violation of NAAQS?
YES
NO
Would source impact any Class I area?
YES
NO
Exempt from
● Air quality review
● Monitoring
● Visibility, soils, vegetation review
Subject to full PSD review
ABBREVIATION CODE.
MES = Major emitting facility
PTE = Potential to emit (including emission controls)
PSD = Prevention of significant deterioration
BACT = Best available control technology
NAAQS = National ambient air quality standard
MES pollutant = a pollutant for which source is a "major source"
De minimis rate = sulfur dioxide 10 tons/yr
particulate matter 10 tons/yr
SO_2 sulfur dioxide
PM = particulate matter

Figure 8-4. PSD Applicability Chart

new source, all methods giving lower emissions must be shown to be inappropriate in terms of cost, energy impact, or technical feasibility.

Nonattainment Requirements--The requirements for permitting a source which will emit significant levels of a pollutant for which the area is not in attainment of the NAAQS are quite stringent. First, the source must use the Lowest Achievable Emission Rate (LAER). It must then offset the resulting emissions by reducing emissions from another source in the area by a more than equivalent amount. There are additional requirements relating to the other sources owned by the applicant and to assuring a net positive air quality improvement, but these are not pertinent to this discussion.

LAER is defined as the strictest control technology required for this type of source by any State Implementation Plan (SIP), or the lowest emissions achieved by any operating source of the same type, whichever is more stringent unless the owner or operator of the proposed source demonstrates that such limitations are not achievable. This does not take cost or any other side effects into account. It also recognizes the transfer of control technology from one type of source to another, if technically feasible.

The resulting emissions after LAER must be offset on a pollutant-by-pollutant basis by reducing emissions from other sources in the area. For nonreactive pollutants the offset must be from another source in the immediate vicinity. For NO_x and hydrocarbons, however, offsets can be obtained over a broader area. The offsetting emission reduction must be greater than the emissions from the new source, thus causing a net positive air quality improvement.

Effects of New Source Reviews on the Environmental Impacts of Refineries--The effects of the New Source Review process on the environmental impacts of refineries should be significant. Any new refinery permitted under this system should have much lower emissions than existing refineries. This would be particularly true in the area of hydrocarbon emissions, but it would also occur for NO_x and SO_2.

The NSR process will also discourage expansion in nonattainment areas, where the combined impacts of a heavily industrialized area have already caused a deterioration in air quality. If an expansion were to be made in such an area, it could only be done by achieving a greater than equivalent offset. Thus, the impetus to build new facilities can provide the impetus to clean up older facilities. The net effect of these policies should be an improvement in existing air quality.

8.5.3 Potential Regulations and Policies

There are many standards and regulations currently under consideration that would have a significant impact on refinery emissions. It would be quite difficult to document all of these since many have not even been published as proposals at this time. Several examples will be discussed in this section to illustrate regulatory trends. Caution should be used in interpreting or applying these regulations since they are only proposed at this point, and they may be significantly modified before being adopted.

State Regulations--Only the new and developing standards for the Bay Area (San Francisco) and the South Coast (Los Angeles) regions of California are summarized here. Other regulatory agencies may be similarly updating their standards. Most of these new and proposed standards are concerned with the emission of hydrocarbons from refineries.

Two levels of control for SO_x emissions from catalytic cracker catalyst regeneration are being considered by the South Coast Region, one of which is expected to become a standard by 1982. One proposed standard calls for replacement of the conventional catalyst with a newly developed catalyst which can reduce SO_x emissions by 80 percent without additional controls; the other proposed the addition of alkaline scrubbers for 90 percent control of SO_x. The South Coast Region also proposes that the allowable sulfur content of fuels be halved by 1982.

Many of the proposed standards for the Bay Area and South Coast Regions are concerned with fugitive emissions, an area not emphasized by present standards. The South Coast Region proposes that by 1980, leak rates, maintenance schedules, etc. for random hydrocarbon emissions be established. Pumps and compressors within 3 miles of the control center would be inspected every eight hours, all others every 24 hours.

The South Coast Region also proposes that natural gas-fired control devices such as afterburners must have a stand-by fuel system for use during natural gas curtailment. By 1980, all relief valves would be vented to vapor recovery or disposal. By 1982, combustion modification and/or ammonia injection for control of NO_x would be required on heaters and boilers.

A Bay Area Region standard which went into effect in December 1979, limits valve leakage to 10,000 ppm VOC measured one centimeter from the leak. It is proposed that this standard be applied also to flanges.

By March 1980, emissions from condensers or vacuum-producing systems must be incinerated, compressed and added to fuel gas, or controlled equivalently. It is proposed that emissions from steam ejectors be similarly controlled.

Also by March 1980, hot wells and/or accumulators associated with contact (barometric) condensers must be covered and the organic vapors either incinerated or contained and treated. It is proposed that this standard apply to the hot wells and/or accumulators associated with all condensers.

Emissions from process vessel depressurizing must, by 1980, be passed through a knockout pot to remove condensable hydrocarbons, then incinerated, flared, or compressed and added to the fuel gas. It is proposed that emissions from process vessel purging be similarly controlled.

Another Bay Area Region standard effective March 1980, is similar to those in several other states: oil/water separators must have a solid cover, a floating pontoon or double-deck cover, 90 percent effective vapor recovery, or other approved control equipment.

Federal Standards--Petroleum refineries are among those industries for which New Source Performance Standards (NSPS) will be formulated or updated in the near future. It is expected that within 2-3 years additional standards will be added to Subpart J of 40 CFR Part 60 and parts of the existing Subpart J may be revised. Additional standards may concern such emissions as SO_x from catalytic cracking catalyst regeneration and fugitive emissions.

Effects of Potential Regulations and Policies on the Environmental Impacts of Refineries--These proposed regulations will tend to bring more uniformity to the determination of BACT. They do not generally increase the stringency of measures already required through the New Source Review process. If other states follow California lead in upgrading their SIP's, however, the allowable emissions from existing refineries could be greatly reduced, with a corresponding reduction in the environmental impacts of those refineries. Such stringency in state regulations may or may not be warranted, depending on the magnitude of any air quality problems in the specific state.

8.6 Effects of New and Developing Technology

Although petroleum refining is considered a mature technology area, it is constantly undergoing a process of improvements. The environmental impacts of refineries will be reduced in the future through new developments in both process technology and emission control technology.

8.6.1 Process Technology

Process technology in petroleum refining has continually evolved to meet the demands of the end-use sector. Some of the current evolutionary trends in refining include the shift to produce lead-free gasoline, increased use of hydrodesulfurization to achieve lower fuel sulfur contents, and a push for greater energy efficiency. Some of these trends will tend to aggravate emissions while others will reduce them.

The production of lead-free gasoline requires significantly more processing in units like catalytic reformers, alkylation units, and isomerization units. While the units are not major emitters, they do contribute to fugitive emissions and emissions from combustion sources. Since there is a decrease in gasoline range yields with this type of processing, more crude must be charged to maintain the same gasoline production. This will cause slight increases in emissions across the board. Much of this effect is now behind us, but a phase-down of gasoline pool lead content will cause continued emissions increases.

Sulfur levels in many fuels are being regulated downward. This will require an increased use of hydrodesulfurization to achieve these low sulfur levels, which will, in turn, increase the load on Claus plants and tail gas treating units. The hydrogen demand will also begin to exceed that provided by catalytic reforming, and thus require construction of hydrogen plants. Both of these effects will tend to cause an increase in refinery emissions unless countered by more effective control technology.

The trend toward greater use of energy conservation will tend to reduce the emissions from combustion sources. The recovery of process heat and the use of intrinsically more efficient processes will reduce the heat required from process heaters and steam boilers. Since the emissions from combustion equipment are proportional to the fuel burning rate, this should result in an emission reduction.

8.6.2 Emission Control Technology

New and improved emission control technology will continue to appear in petroleum refining. Significant reductions may be achieved by application of technology, such as covers for API separators, scrubbers for flue gas from fluid catalytic cracking, and combustion modifications to reduce NO_x. These effects could be complemented by progress on developing technologies like the fluid cracking catalyst which adsorbs SO_x from the regenerator.

One area with great potential for improved technology is in fugitive emission control. The manufacturers of seals, packing, and gaskets for process equipment have designed their products to meet the users needs. Up until now, those needs have been to limit product loss and maintain safe operation. No one was aware or concerned about "low level" fugitive vapor leaks which could not be detected visibly. Fugitive emission regulations will provide the incentive to develop more effective seals, packing, etc., and will result in lower emissions and lower costs for monitoring and maintenance programs.

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10.0 CONVERSION FACTORS

To Convert From	To	Multiple By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
lb/10^6 Btu	g/Mcal	18.0
grain/ft^3	g/m^3	2.29
gal/$10^6 ft^3$	ℓ/$10^6 m^3$	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mg/ℓ	119.8